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THIRTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1905.

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THE year 1905 has been remarkably prolific in determinations of atomic weight, and much of the work done was of unusually high quality. Some of the published researches deal with revisions of the more fundamental values, such as the atomic weights of nitrogen, chlorine, iodine, sodium and potassium. These investigations have made it clear that a general revision and recalculation of all the atomic weights is now needed, and the developments of the next year or two are likely to bring about many changes in the accepted table. Meanwhile, the International Committee[1] advocates a conservative policy, and recommends that changes be deferred until important work, now known to be in progress, shall have been completed. Then the table of atomic weights, as presented in their report, can be revised intelligently, whereas such a revision, undertaken now, would be premature. The determinations published during 1905 are given in the following pages.

NITROGEN.

Guye,[2] from the density and critical constants of nitrous oxide, finds N = 14.006. Jaquerod and Scheuer,[3] from densities and

[1] See report in this Journal for January, 1906.

[2] Compt. rend. 140, 1241.

[3] Ibid. 140, 1384.

compressibilities of several gases, have determined the following molecular and atomic weights:

$$H = 1.0078.$$

$$NO = 30.005, \text{ whence } N = 14.005.$$

$$NH_3 = 17.014, \text{ whence } N = 13.991.$$

Jaquerod and Perrot,[1] from the density of nitrogen at 1067°, find N = 14.008. Guye and Pintza[2] determined the normal weight per liter of ammonia, nitrous oxide, and carbon dioxide.[3] The figures for NH_3 and N_2O are as follows:

NH_3.	N_2O.
0.77080	1.97762
0.77069	1.97707
0.77073	1.97760
0.77099	
0.77076	

From nitrous oxide, compared with carbon dioxide in corresponding states, N = 14.006. From the critical constants, N = 14.008. Lord Rayleigh,[4] from the density of nitrous oxide under very small pressures, found $N_2O = 43.996$, whence N = 13.998.

Guye and Davila[5] prepared nitric oxide by three different methods, and determined its density. The weight of one liter, at Geneva, under normal conditions, is given below. The three columns relate to the three preparations.

1.	2.	3.
1.3406	1.3403	1.3399
1.3402	1.3398	1.3403
1.3401	1.3400	
1.3407	1.3408	
1.3398	1.3402	
1.3402	1.3402	

If the weight of one liter of oxygen is 1.4290 grams, the ratio $NO : O_2$ gives NO = 30.012. Corrected by physico-chemical methods, N = 14.006 to 14.010, according to the method employed.[6]

Nitric oxide was also the substance chosen by R. W. Gray[7]

[1] Compt. rend. 140, 1542.

[2] Ibid. 141, 51.

[3] See under Carbon, later.

[4] Phil. Trans. 204, 369; Pr. Roy. Soc. 74, 446.

[5] Compt. rend. 141, 826.

[6] For the method of correction by critical constants, see Guye: J. chim. phys. 3, 321.

[7] J. Chem. Soc. 87, 1601.

for his determinations of the atomic weight of nitrogen. First, its density was determined in comparison with oxygen, by weighing both gases in the same bulb under corresponding conditions. The following weights were observed at Bonn, where the bulb was filled at 0° and 760 mm.

	NO.	O_2.
Series I.	0.35845	0.38230
	0.35852	0.38229
	0.35851	0.38227
	0.35849	0.38225
	0.35848	0.38226
	0.35856	0.38230
Mean,		0.38228
Series II.	0.35851	
	0.35848	
	0.35852	
	0.35850	
Mean,	0.35851	
dupplementary Seterminations[1]	0.35848	
	0.35855	

The direct ratio between these weights is $O_2 : NO = 32 : 30.010$, whence N = 14.010. Corrected by the method of limiting densities, N = 14.004; by the critical constants, 14.008. Mean value, N = 14.006.

Gray effected the gravimetric analysis of nitric oxide by burning finely divided nickel in the gas. Two sets of determinations were made, with nickel from different sources. In the first series, occluded nitrogen in the resultant nickel oxide was determined, and a correction for it was applied. In the second series the occluded gas was expelled by heating. Only the *corrected* weights are given below.

	Weight NO.	Weight O.	Weight N.
Series I.	0.31384	0.16729	——
	0.64304	0.34300	0.29920
	0.50672	0.27025	——
Series II.	0.54829	0.29221	——
	0.61862	0.32981	0.28885
	0.62622	0.33401	0.29234
	0.62128	0.33111	——
	0.54469	0.29029	0.25432
	0.52001	0.27715	0.24270
	0.62103	0.33103	0.28998

[1] Made in London, but corrected to the latitude of Bonn.

From these weights the following values for the atomic weight of nitrogen are derived:

	Ratio $NO:O_2$.	Ratio $N_2:O_2$.	Ratio $NO:N_2$.
I.	14.016	——	——
	13.996	13.999	14.001
	14.000	——	——
II.	14.022	——	——
	14.011	14.013	14.015
	13.998	14.004	14.009
	14.021	——	——
	14.009	14.017	14.014
	14.020	14.011	14.003
	14.017	14.012	14.011
		Mean of all, 14.010	

The gas remaining after the combustion of the nickel, was pure nitrogen, and two density comparisons of it with oxygen were made:

Weight N_2.	Weight O_2.
0.32286	0.36889
0.32275	0.36879
Mean, 0.32280	0.36884

From direct comparison of these figures, N = 14.003. Corrected by the method of limiting densities, N = 14.008. From the mean of all his determinations Gray puts N = 14.0085, or, rounded off, 14.01.

The agreement between all these new values for N, whether gravimetric or physico-chemical, is very striking. In a very complete summary of all the data relative to the atomic weight of nitrogen, Guye[1] has discussed the sources of error in the different methods of determination, and has made it quite clear that the true figure cannot exceed 14.01. The Stas value, 14.04, seems certainly to be high, although the source of error in it remains to be ascertained. The higher value, however, was obtained in two analyses of silver trinitride, AgN_3, by A. W. Browne,[2] who promises further determinations. In Guye's summary the possibility of a change in the atomic weight of silver is indicated;

[1] Bull. soc. chim. August, 1905, with independent pagination. Another paper by Guye is in Compt. rend. 140, 1387.

[2] This Journal, 27, 554.

but that, so far, is only a suggestion. Hinrichs,[1] in a brief criticism of recent work, argues in favor of N = 14.

CHLORINE.

Two important memoirs on the atomic weight of chlorine appeared during 1905. First, Dixon and Edgar[2] have effected a direct comparison between hydrogen and chlorine. Hydrogen was weighed in palladium. Chlorine, prepared by the electrolysis of fused silver chloride, was weighed in liquid form. The two elements, with chlorine slightly in excess, were made to unite in a glass bulb; the excess of chlorine remaining after union was caused to liberate iodine from a solution of potassium iodide, and then determined by titration with sodium thiosulphate. The corrected data, reduced to a vacuum standard, are given in the following table:

Weight H.	Weight Cl.	Atomic weight Cl.
0.9993	35.1666	35.191
1.0218	35.9621	35.195
0.9960	35.0662	35.207
1.0243	36.0403	35.185
1.0060	35.4144	35.203
0.9887	34.8005	35.198
1.0159	35.7639	35.204
1.1134	39.1736	35.184
1.0132	35.6527	35.188
		Mean, 35.195±0.0019

This, of course, refers to hydrogen as unity. If O = 16, Cl = 35.463. Additional determinations, to include the weight of the hydrochloric acid produced, are promised.

These determinations by Dixon and Edgar have the peculiar merit of directness. Chlorine is referred to one of the fundamental standards, without the intervention of any other element, although the method employed is one of great experimental difficulty, and therefore subject to undiscovered errors. On their face, however, the results are entitled to receive very high weight.

The work of Richards and Wells,[3] on the other hand, is indirect, at least so far as the atomic weight of chlorine is concerned. In

[1] Compt. rend. 140, 1590.

[2] Phil. Trans. 205, 169. Series A.

[3] This Journal, 27, 459. Original in Publication 28 of the Carnegie Institution.

their research the synthesis of silver chloride was effected, by two distinct processes, and from the data so obtained, the atomic weight of silver being assumed, that of chlorine was calculated.

Some of the syntheses were performed by dissolving silver in nitric acid, precipitating as chloride, and weighing the latter in a Gooch crucible. In other cases the nitrate was converted into chloride in a quartz dish, dried therein, and weighed without transfer of material. All weights, of course, were reduced to a vacuum, and many corrections were carefully determined and applied. The corrected results from two series, are as follows: For details the original memoir must be consulted. The brackets indicate sub-series involving the use of different samples of silver.

PRELIMINARY SERIES.

Weight Ag.	Weight AgCl.	Ratio, 100 Ag : AgCl.
9.06483	12.04365	132.861
8.39217	11.14985	132.860
5.37429	7.14056	132.865
8.08222	10.73869	132.868
7.08517	9.41362	132.864
7.97715	10.59837	132.859
8.11978	10.78767	132.857
8.53452	11.33907	132.861
6.73284	8.94511	132.858
8.91366	11.84240	132.857
9.72295	12.91769	132.858
8.63961	11.47862	132.860
11.13795	14.79849	132.865
		Mean, 132.861

FINAL SERIES.

Weight Ag.	Weight AgCl.	Ratio, 100 Ag : AgCl.
7.24427	9.62508	132.865
8.30502	11.03484	132.870
7.29058	9.68676	132.867
8.58472	11.40614	132.866
8.01318	10.64648	132.862
9.77160	12.98335	132.868
7.98170	10.60528	132.870
11.49983	15.27964	132.868
6.25318	8.30834	132.866
7.72479	10.26360	132.866
		Mean, 132.867
		Stas found, 132.848

From the final series, if Ag = 107.92, Cl = 35.470. If Ag = 107.93, Cl = 35.473. The authors indicate a preference for the lower value for silver. In either case the value for chlorine is higher than the hitherto accepted 35.455; and its adoption will compel many corrections to be made in the general atomic weight table. The research of Richards and Wells is a model of painstaking accuracy.

From the density and critical constants of hydrochloric acid, Guye[1] finds the molecular weight HCl = 36.484, whence Cl = 35.476. A new determination of the density of chlorine gas has lately been published by Treadwell[2] but not yet applied to the calculation of its molecular weight.

BROMINE.

In his research upon the atomic weight of iodine, Baxter[3] made a series of experiments upon the conversion of silver bromide into chloride, by heating in a current of dry chlorine. Vacuum weights are given in the following table, and reduced with Ag = 107.93 and Cl = 35.473.

Weight AgBr.	Weight AgCl.	Atomic weight Br.
10.92091	8.33538	79.955
13.88062	10.59457	79.951
8.21484	6.27006	79.952
7.87887	6.01352	79.956
6.90106	5.26735	79.951
9.53704	7.27926	79.952
		Mean, 79.953

This is sensibly identical with the generally accepted value, 79.955.

IODINE.

An important continuation of the research upon iodine, which was reported in 1904, has been published by Baxter.[4] First, silver iodide was converted into bromide by heating in bromine. The corrected data are as follows:

[1] Compt. rend. **140**, 1241.
[2] Z. anorg. Chem. **47**, 446.
[3] This Journal, **27**, 884.
[4] Ibid. **27**, 876.

Weight AgI.	Weight AgBr.	Atomic weight I.
13.65457	10.92091	126.985
17.35528	13.88062	126.987
9.70100	7.75896	126.982
10.27105	8.21484	126.983
9.85688	7.88351	126.986
8.62870	6.90106	126.991
11.92405	9.53704	126.981
7.56933	6.05389	126.987
		Mean, 126.985

Atomic weights calculated with Ag = 107.93, Br = 79.955.

Two new series of determinations were made of the ratio AgI : AgCl. The first of these was upon the weights of iodide given in the foregoing table. That is, the bromide, after weighing, was transformed into chloride.

SERIES II.

Weight AgI.	Weight AgCl.	Atomic weight I.
13.65457	8.33538	126.985
17.35528	10.59457	126.983
10.27105	6.27006	126.980
8.62870	5.26735	126.985
11.92405	7.27926	126.976
		Mean, 126.982

SERIES III.

Weight AgI.	Weight AgCl.	Atomic weight I.
9.26860	5.65787	126.990
6.72061	4.10259	126.984
11.31825	6.90912	126.987
10.07029	6.14754	126.979
13.49229	8.23649	126.980
		Mean, 126.984

Three additional series of measurements relate to the ratio between silver and iodine. In the first one, iodine and silver were weighed separately; the iodine was then converted into hydriodic acid, and precipitated by known quantities of silver.

Weight I.	Weight Ag.	Atomic weight I.
3.29308	2.79897	126.983
3.70132	3.14584	126.988
3.75641	3.19258	126.991
3.24954	2.76186	126.988
4.12541	3.50639	126.984
3.53166	3.00165	126.988
2.99835	2.54842	126.985
2.00015	1.69991	126.993
		Mean, 126.987

In five of these experiments the silver iodide was collected and weighed, with the subjoined results.

Weight I.	Weight AgI.	Atomic weight I.
3.75641	6.94913	126.987
3.24954	6.01137	126.989
4.12541	7.63204	126.977
3.53166	6.53351	126.979
2.99835	5.54682	126.983
		Mean, 126.983

Finally, in order to determine the ratio Ag:AgI, the filtrate and washings from the previous sets of analyses were examined for the silver they might contain. This gave a small correction to the weights already cited, with results as follows:

Weight Ag.	Weight AgI.	Atomic weight I.
3.19249	6.94877	126.990
2.76175	6.01110	126.986
3.00189	6.53399	126.993
2.54833	5.54659	126.986
		Mean, 126.989

The final value, adopted by Baxter, is I = 126.985, when Ag = 107.93 and Cl = 35.473. Vacuum weights are given throughout the memoir. Two short critical papers on iodine, by Ladenburg[1] and Koethner[2] respectively, have also appeared during the year. They contain no new determinations.

SODIUM.

The determinations of the atomic weight of sodium by Richards and Wells,[3] cover the measurement of two ratios. It goes without saying that in all of Richards' work every conceivable precaution is taken, and every correction applied. The data obtained appear in the two following tables:

[1] Ann. 338, 259.

[2] Ibid. 338, 262.

[3] This Journal, 27, 459. Original in Publication 28 of the Carnegie Institution.

RATIO NaCl : AgCl.

Weight NaCl.	Weight AgCl.	Ratio, 100 AgCl : NaCl.
3.27527	8.03143	40.781
5.56875	13.65609	40.779
4.18052	10.25176	40.779
4.54319	11.14095	40.779
1.97447	4.84190	40.778
3.97442	9.74547	40.782
6.69495	16.41725	40.780
2.88692	7.07955	40.778
5.56991	13.65833	40.780
5.85900	14.36693	40.781
		Mean, 40.780

RATIO Ag : NaCl.

Weight NaCl.	Weight Ag.	Ratio, 100 Ag : NaCl.
3.96051	7.30896	54.187
2.32651	4.29355	54.186
5.36802	9.90699	54.184
4.00548	7.39210	54.186
4.69304	8.66101	54.186
3.27189	6.03842	54.185
5.08685	9.38795	54.185
3.66793	6.76952	54.183
5.48890	10.12993	54.185
3.55943	6.56909	54.185
		Mean, 54.185

Two supplementary analyses for fixing the foregoing ratio were made with salt and silver which had both been fused in vacuo.

NaCl.	Ag.	Ratio.
3.38684	6.25046	54.185
4.68529	8.64634	54.188

With Ag = 107.92 and Cl = 35.470 we have for Na, from AgCl ratio, Na = 23.004. From Ag ratio, Na = 23.007. With Ag = 107.93 and Cl = 35.473, Na = 23.008.

POTASSIUM.

Atomic weight redetermined by Archibald,[1] from analyses of the chloride. Two ratios were measured. The data given below represent vacuum weights.

[1] Trans. Roy. Soc. Canada, 1904, Section III, p. 47.

RATIO AgCl : KCl.

Weight AgCl.	Weight KCl.	Ratio.	Atomic weight K.
4.25916	2.21586	52.028	39.142
3.83250	1.99379	52.023	39.138
5.57396	2.89977	52.025	39.139
9.10362	4.73606	52.026	39.140

RATIO Ag : KCl.

Weight Ag.	Weight KCl.	Ratio.	Atomic weigh K.
3.20598	2.21586	69.116	39.142
2.88479	1.99379	69.114	39.140
4.19557	2.89977	69.115	39.141
6.85280	4.73606	69.111	39.137

In mean, K = 39.140, when Ag = 107.93 and Cl = 35.455. With Cl = 35.473 this becomes K = 39.122.

CARBON AND GLUCINUM.

Parsons[1] has rediscussed his analyses of the basic acetate and acetylacetonate of glucinum, which were noticed in the report for 1904. Combining the two equations yielded by the two observed ratios, and solving algebraically, the following values were simultaneously determined:

$$Gl = 9.112.$$
$$C = 12.007.$$

From the density and critical constants of CO_2, Guye[2] finds C = 12.003, and from C_2H_2, C = 12.002. Jaquerod and Perrot,[3] by comparing the densities of gases at 1067°, find the molecular weight of CO to be 28.009, and of CO_2 43.992. Hence C = 12.009 and 11.992.

Guye and Pintza[4] have also determined anew the density of carbon dioxide. One liter at normal temperature and pressure weighs—1.97684, 1.97676, 1.97681 grams.

Lord Rayleigh,[5] studying the compressibility of gases, has deduced several molecular weights from measurements of density at ordinary pressures and very small pressures. The subjoined data refer to carbon monoxide and dioxide, when $O_2 = 32$.

	Atmospheric P.	Very small P.
Carbon monoxide.....	28.000	28.003
Carbon dioxide.....	44.268	44.014

[1] This Journal, 27, 1204.
[2] Compt. rend. 140, 1241.
[3] Ibid. 140, 1542.
[4] Ibid. 141, 51.
[5] Phil. Trans. 204, 369.

From the figures in the second column CO—O gives C = 12.003. CO_2—O_2 = 12.014, $2CO_2$—CO = 11.992. From the density of hydrogen at very small pressures, H_2 = 2.0173.

STRONTIUM.

In 1894 Richards published his determinations of the atomic weight of strontium, which were based upon analyses of the bromide. A little later he made another set of measurements upon the chloride, which did not accord sufficiently well with the bromide series. The discrepancy is now explained by the discovery that the then accepted value for chlorine was too low, and the actual work upon strontium chloride has proved to be satisfactory. The data now published by Richards[1] are given below. They represent vacuum weights, and refer to Ag = 107.93 and Cl = 35.473.

Weight $SrCl_2$.	Weight Ag.	Ratio, 100 Ag_2 to $SrCl_2$.
4.2516	5.7864	73.476
2.4019	3.2688	73.480
3.5184	4.7886	73.475
3.0264	4.1189	73.476
		Mean, 73.477

Hence Sr = 87.661 as compared with 87.663 from the bromide.

COPPER.

Incidentally to his work on the atomic weight of tellurium, Gallo[2] made a few electrolytic precipitations of copper in comparison with silver. The corrected data are as follows:

Weight Cu.	Weight Ag.	Atomic weight Cu.
0.21805	0.73937	63.66
0.27153	0.92062	63.65
0.19001	0.64571	63.52
0.39585	1.34578	63.50
		Mean, 63.58

CADMIUM.

Baxter and Hines,[3] in redetermining the atomic weight of cadmium, have made use of the chloride. Both of the usual ratios were measured, and the corrected data reduced to vacuum weights are given below.

[1] Pr. Am. Acad. 40, 603; Z. anorg. Chem. 47, 145.

[2] Gazz. Chim. Ital. 35, 261. Atomic weight computed with Ag=107.93.

[3] This Journal, 27, 222.

RATIO $CdCl_2$: 2AgCl.

Weight $CdCl_2$.	Weight AgCl.	Atomic weight Cd.
5.53241	8.65356	112.475
7.77758	12.16166	112.471
8.87917	13.88344	112.481
		Mean, 112.476

RATIO $CdCl_2$: 2Ag.

Weight $CdCl_2$.	Weight Ag.	Atomic weight Cd.
4.92861	5.80063	112.463
3.86487	4.54891	112.454
5.08551	5.98569	112.451
5.84335	6.87704	112.468
5.99952	7.06084	112.468
3.73092	4.39095	112.467
		Mean, 112.462

The calculations were made with Ag = 107.93 and Cl = 35.473. Additional data are promised, relative to cadmium bromide. The mean of the two series, as given by Baxter and Hines, is Cd = 112.469.

ALUMINUM.

The work of Kohn-Abrest on the atomic weight of aluminum was noticed in the report for 1904. It has since been published in detail.[1] Impure aluminum, but containing known impurities, was dissolved in hydrochloric acid, and the hydrogen evolved was burnt over copper oxide and weighed as water. The following, uncorrected amounts of water were furnished by 100 parts of the metal.

98.08
98.20
97.86
98.10
98.44
98.03
97.98

The mean, corrected for the impurities in the aluminum, is 99.151. Hence Al = 27.05 when H = 1. With O = 16, Al = 27.25.

Two additional experiments were made upon the conversion of aluminum into oxide, as follows:

0.3429 Al gave 0.6444 Al_2O_3. Al = 27.09.
0.4168 Al gave 0.7850 Al_2O_3. Al = 27.03.

[1] Bull. soc. chim. [3] 33, 121.

The degree of concordance shown by these determinations is not satisfactory; neither were the methods by any means unimpeachable.

SILICON.

The determination of the atomic weight of silicon by W. Becker and J. Meyer,[1] was effected through the conversion of silicon tetrachloride into the dioxide. The chloride was decomposed by ice water, under suitable precautions, which are fully described. After decomposition the mixture was evaporated to dryness, and the silica was ignited and weighed. In a supplementary investigation by Meyer[2] the possible retention of chlorine by the silica was carefully examined, and that impurity was proved to be absent. The final data, referred to vacuum weights, are given below, as published in the second of the two papers. The atomic weight was computed with Cl = 35.470.

Weight $SiCl_4$.	Weight SiO_2.	Atomic weight Si.
4.16733	1.47597	28.259
4.69585	1.66304	28.253
4.91918	1.74204	28.248
5.37434	1.90349	28.260
5.93985	2.10364	28.254
6.73605	2.38570	28.257
7.16361	2.53606	28.220
7.82779	2.77242	28.259
Sum, 46.82400	16.58236	Mean, 28.251

The value adopted by Meyer is Si = 28.25. This is lower than the 28.4 derived from Thorpe and Young's analyses of the bromide.

LEAD.

In an interesting paper upon the lead voltameter, Betts and Kern[3] give two series of determinations of the electrochemical equivalent of lead. The metal was deposited in direct electrolytic comparison with silver, from an acid solution of lead fluosilicate. The weights deposited and the corresponding equivalents were as follows, the atomic weight of silver being taken as 107.93.

[1] Z. anorg. Chem. 43, 251.

[2] Ibid. 47, 45.

[3] Trans. Amer. Electrochem. Soc. 6, 67.

FIRST SERIES.

Weight Ag.	Weight Pb.	Equivalent Pb.
5.8958	5.6221	102.90
5.8958	5.6396	103.24
5.7863	5.5246	103.04
5.7863	5.5450	103.43
7.8408	7.5108	103.39
7.8408	7.5168	103.47
7.6253	7.3191	103.59
7.6253	7.3221	103.62
6.2287	5.9600	103.27
6.2287	5.9605	103.28
16.6804	15.9996	103.52
16.6804	16.0014	103.54
6.8652	6.5815	103.47
6.8652	6.5812	103.46
9.3253	8.9390	103.46
9.3253	8.9419	103.49
6.8566	6.5695	103.41
6.8754	6.5877	103.41

SECOND SERIES.

Weight Ag.	Weight Pb.	Equivalent Pb.
9.0470	8.6678	103.41
9.0470	8.6663	103.39
13.4113	12.8607	103.49
13.4113	12.8558	103.46
7.2780	6.9716	103.39
7.2780	6.9755	103.44
7.2738	6.9695	103.41
7.2738	6.9698	103.42
6.5278	6.2550	103.42
6.4864	6.2168	103.44

The mean of the determinations in the first series gives an equivalent of 103.39, or Pb = 206.78. From the second series Pb = 207.86. As the object of the investigation was to ascertain the availability of the lead voltameter for exact work, and not to determine an atomic weight, these values cannot be utilized directly. They show, however, some promise, and indicate that the process used might be developed into a good method of determination. The suggestiveness of the data warrants their reproduction here.

TELLURIUM.

The electrochemical equivalent of tellurium has been determined by Gallo,[1] in comparison with silver taken as Ag = 107.93.

[1] Atti Accad. Lincei, [5] 14, 23, 104; Gazz. chim. ital. 35, 245.

Three series of determinations are given, with weights reduced to a vacuum. The data are as follows:

Weight Ag.	Weight Te.	Atomic weight Te.
0.74117	0.218412	127.22
1.03801	0.304514	126.65
0.91704	0.27256	128.30
1.041101	0.307117	127.35
1.09064	0.321952	127.42
1.16302	0.34582	128.16
0.968903	0.28646	127.64
1.518712	0.44767	127.28
0.906561	0.26836	127.76
0.995511	0.29586	128.28
0.86596	0.25656	127.90
1.11282	0.328318	127.44
		Mean, 127.617

Although these values are widely variable, the mean approaches closely to the atomic weight as determined by other investigators.

Gutbier's[1] redetermination of the atomic weight of tellurium is based upon the reduction of scrupulously purified tellurium dioxide by two distinct methods. In the first series of experiments the dioxide, mixed with finely divided silver and quartz sand, was reduced by pure hydrogen. In the second series, hydrazine was the reducing agent. The data, with vacuum weights, are as follows:

HYDROGEN SERIES.

Weight TeO_2.	Weight Te.	Atomic weight.
2.99688	2.39585	127.55
1.30740	1.04527	127.60
2.04325	1.63380	127.68
2.61725	2.09249	127.59
3.61725	2.89222	127.65
		Mean, 127.614

HYDRAZINE SERIES.

Weight TeO_2.	Weight Te.	Atomic weight.
1.90601	1.52390	127.62
1.03532	0.82784	127.67
2.2200	1.77480	127.55
		Mean, 127.613

[1] Ann. 342, 266.

Gutbier thus reaches the same value for tellurium as Gallo, which may be rounded off to 127.6. This is the value adopted in the international table.

BISMUTH.

In a doctoral dissertation by Lothar Birckenbach,[1] some experiments are described involving the synthesis of bismuth trioxide from the metal, and also the reduction of the oxide to metal. The bismuth was from several distinct sources, and included material received from Classen, whose determinations of this atomic weight were published several years ago.

In the first part of the research, bismuth was oxidized by means of nitric acid, in porcelain crucibles. The oxide was tested for occluded gases, which were proved to be absent, or at least present in only insignificant traces. Three series of determinations are given, representing different samples of bismuth, with the subjoined results.

Weight Bi.	Weight Bi_2O_3.	Atomic weight.
9.63289	10.74328	208.22
10.41101	11.61288	208.04
10.97914	12.24528	208.11
10.1199	11.2880	208.10
18.96770	21.15541	208.08
11.99601	13.38001	208.01
27.23022	30.37392	207.88
24.9817	27.86431	207.99
10.11284	11.27998	207.94
28.35991	31.63053	208.10
		Mean, 208.05

By reduction of bismuth trioxide in a stream of ammonia gas, with precautions which are fully described in the original memoir, the following determinations were made:

Weight Bi_2O_3.	Weight Bi.	Atomic weight.
1.45827	1.30751	208.14
2.12432	1.90461	208.04
3.0021	2.6918	207.92
2.1012	1.8840	208.17
3.0182	2.70620	208.16
1.9091	1.71171	208.02
		Mean, 208.08

[1] Ueber das Atomgewicht des Wismuths. Inaugural-Dissertation, Erlangen, 1905.

Birckenbach concludes, from all the determinations, that Bi = 208 approximately, and not 209 as measured by Classen.

The foregoing investigation was conducted under the direction of Gutbier, who has carried the work still farther. In a preliminary notice Gutbier[1] states that eight analyses of bismuth bromide gave values for Bi ranging from 207.89 to 208.24, in mean 208.05. Additional determinations are being made.

PALLADIUM.

In the elaborate memoir by Amberg[2] on the atomic weight of palladium, several methods of determination are described; but all relate to analyses of palladosammine chloride, $Pd(NH_3Cl)_2$.

First, palladium was precipitated by electrolysis, and the chlorine in the remaining solution was weighed as AgCl. From the following data, the atomic weight A is determined by the proportion of Pd, B by the ratio between the original salt and AgCl.

Weight salt.	Weight Pd.	Weight AgCl.	A.	B.
1.06045	0.53609	.....	107.38	....
1.00028	0.50528	1.35867	107.28	106.09
1.66386	0.84085	2.25437	107.33	106.59
0.83195	0.42092	1.12282	107.56	107.45
1.91591	0.96886	2.59799	107.44	106.45

In a second series of experiments the palladium was thrown down by hydrazine sulphate; in other respects this series is like the first.

Weight salt.	Per cent. Pd.	Weight AgCl.	Atomic weight.
1.32423	50.12	1.78656	107.52
1.02642	50.29	1.39247	106.35
1.30335	50.36	1.76875	106.28
1.59709	...	2.16641	106.37
1.88622	50.49	2.55028	107.06
2.59665	50.68	3.51783	106.64

From the sum of all the chlorine determinations, Pd = 106.67, when Ag = 107.93, Cl = 35.45, N = 14.04 and H = 1.008. The weights are referred to a vacuum.

In the final series of determinations, palladium was electrolytically precipitated from a sulphuric acid solution of the palladosammine chloride, with the aid of a rotating anode. Twelve analyses were made, with three separate preparations of the chloride, and with the subjoined results:

[1] Z. Elektrochem. 11, 831.

[2] Ann. 341, 235.

Weight salt.	Weight Pd.	Per cent. Pd.	Atomic weight.
0.62446	0.31470	50.396	106.70
0.83878	0.42280	50.407	106.75
1.50282	0.75725	50.389	106.67
1.06704	0.53753	50.385	106.66
1.98342	0.99971	50.403	106.74
1.53093	0.77153	50.396	106.71
1.18995	0.59971	50.398	106.71
0.62635	0.31572	50.406	106.75
1.76110	0.88739	50.388	106.67
3.79639	1.91298	50.389	106.68
3.97553	2.00333	50.392	106.69
4.62100	2.32834	50.386	106.66
Sum, 23.51777	11.85109		Mean, 106.699

From the sums of the weights, Pd = 106.688. The probable value, derived from all the data, is put by Amberg at 106.7. If recalculated with the new values for N and Cl, 14.01 and 35.473, the figure for palladium will be changed very slightly. The changes due to N and Cl respectively are in opposite directions, and nearly compensate each other.

THORIUM.

R. J. Meyer and A. Gumperz[1] have investigated the supposed complexity of thorium, and have failed to confirm the results announced by Baskerville. First, about 700 grams of thorium nitrate were separated into seven fractions by precipitation with potassium chromate. The fractions were converted into the octohydrated sulphate, which was then applied to the atomic weight determinations. It was weighed first as hydrate, then as anhydrous salt after heating to 400°, and finally ignited to oxide. The data thus obtained are as follows:

Fraction.	Weight hydrate.	Weight $Th(SO_4)_2$.	Weight ThO_2.	Atomic weight.
I	1.2463	0.9301	0.5793	232.4
I	1.3261	0.9927	0.6184	232.5
IV	1.3910	1.0344	0.6442	232.3
IV	1.2543	0.9349	0.5821	232.2
VII	0.8934	0.6680	0.4160	232.3
VII	....	0.4296	0.2676	232.5

Secondly, thorium tetrachloride was fractionally sublimed in a stream of chlorine, and divided into three portions, namely: 1, the most volatile portion, "berzelium;" 2, the medium portion,

[1] Ber. 38, 817.

"new thorium;" 3, the unsublimed residue, "carolinium." These converted into sulphate gave the subjoined data.

Fraction.	Weight hydrate.	Weight $Th(SO_4)_2$.	Weight ThO_2.	Atomic weight.
1	1.2573	0.9199	0.5730	232.5
1	1.0424	0.7647	0.4764	232.6
2	....	1.0650	0.6635	232.4
2	1.0387	0.7758	0.4834	232.7
3	1.1904	0.8824	0.5496	232.4
3	0.7487	0.5545	0.3454	232.4

The mean of all is Th = 232.43. No evidence of a breaking up of thorium was observed, and a spectroscopic examination of the products by Eberhard[1] led to the same conclusion. A brief reply to Meyer and Gumperz was published by Baskerville,[2] in which he urged the importance of observing the exact conditions of his experiments, conditions from which his critics seem to have departed.

The radiothorium described by Ramsay[3] and Hahn[4] should be taken into account in any discussion of the atomic weight of thorium. It was extracted in very small amount from thorianite, and gave about 700,000 times as much emanation as an equal weight of ordinary thoria. Its atomic weight remains to be determined.

METALS OF THE RARE EARTHS.

A considerable number of memoirs upon the rare earths have appeared in the course of the year, with incidental data on the subject of their atomic weights. In only two of them was the determination of atomic weight the principal feature, the paper by Urbain[5] on gadolinium being the most important. Urbain prepared his material by many fractionations of gadolinium nickel nitrate, and analyzed a number of distinct preparations of the octohydrated gadolinium sulphate. According to Eberhard,[6] who has studied several rare earths spectroscopically, Urbain's material for samarium, gadolinium and europium was exceedingly good, if not absolutely free from ad-

[1] Ber. 38, 826.

[2] Ibid. 38, 1444.

[3] J. chim. phys. 3, 617.

[4] Chem. News, 91, 193; 92, 251; Ber. 38, 3371. See also Sackur: Ber. 38, 1756.

[5] Compt. rend. 40, 583.

[6] Z. anorg. Chem. 45, 375.

mixtures. Bettendorff's samarium preparation contained other earths.

For gadolinium, Urbain's data are as follows, calculated with H = 1.007 and S = 32.06.

Fraction.	Weight $Gd_2(SO_4)_3.8H_2O$.	Weight Gd_2O_3.	Atomic weight.
18	1.9256	0.9350	157.35
19	1.9749	0.9589	157.35
19	1.9975	0.9698	157.32
20	2.1083	1.0231	157.15
20	1.8993	0.9214	157.04
21	2.2065	1.0707	157.13
21	1.9535	0.9479	157.12
22	2.2008	1.0685	157.32
22	2.2482	1.0914	157.28
23	2.1932	1.0646	157.25
35	2.0551	0.9974	157.19
36	2.1555	1.0469	157.45
37	2.2277	1.0807	157.04
38	2.2559	1.0946	157.11
39	2.2523	1.0939	157.45
		Mean,	157.24

The value adopted by Urbain, from fractions 18 to 23, is Gd = 157.23.

The paper by Brill[1] describes an attempt to determine atomic weights on very small quantities of material, by means of the microbalance invented by Nernst. In each case a few milligrams of a sulphate, previously heated to 480°, was ignited to oxide. At 480° acid sulphates were destroyed, and the normal salts were stable. The results obtained may be summarized as follows:

Yt.	Er.	Yb.	La.	Sa.	Nd.
89.7	165.6	173.2	139.5	151.2	141.8
89.5	167.5	172.2	139.8	150.5	143.0

These figures, of course, are only approximations; but they indicate the convenience of the method for the ordinary rough determinations which are needed in the identification of the earths.

Feit and Przibylla,[2] in an investigation of the monazite earths, made several determinations of atomic weights by a volumetric method. The weighed oxides were dissolved in a known quantity

[1] Z. anorg. Chem. **47**, 464.

[2] Ibid. **43**, 202.

of standard sulphuric acid, and the excess of the latter was ascertained by titration, with methyl or ethyl orange as indicator. For lanthanum, in a single experiment, the value 139.0 was found.

For neodymium and samarium the following results were obtained:

Nd.	Sa.
144.51	151.20
144.48	151.25
144.53	151.13
Mean, 144.5	Mean, 151.2

Matignon[1] has found that samarium sulphate, heated to about 1000°, is converted into a stable basic salt, Sm_2SO_6. He proposes to use this transformation as a means of determining the atomic weight of samarium. In one experiment, 0.7325 gram of $Sm_2(SO_4)_3$, calcined, at a dull red heat, gave 0.5335 of the basic compound. Hence Sm = 150.6.

According to Urbain,[2] in a communication to the Chemical Society of Paris, the following atomic weights are approximately true. Terbium, 159.5; dysprosium, 162–163; holmium, 140. In a later paper[3] he assigns the value 159.2 to terbium. For an impure terbium preparation Feit[4] found the value 158.6. Emma Potratz,[5] from a preparation of terbium sulphate, found Tb = 153.9, and from another sample 154.2. From the formate she obtained the figure 154, and from the acetate, 153.1. No details are given, but another report is promised in the future.

MISCELLANEOUS NOTES.

From the density and critical constants of sulphur dioxide, Guye[6] has computed its true molecular weight. $SO_2 = 64.065$, and therefore S = 32.065. The molecular weight of argon, determined in the same way, is 39.866. Jaquerod and Scheuer,[7] from the compressibility and density of SO_2, determine its molecular weight as 64.036, whence S = 32.036. Guthe,[8] in a paper upon the silver coulometer, has discussed the electrochemical

[1] Compt. rend. 141, 1230.
[2] Bull. soc. chim. [3] 33, 403.
[3] Compt. rend. 141, 521.
[4] Z. anorg. Chem. 43, 280.
[5] Chem. News, 92, 3.
[6] Compt. rend. 140, 1241.
[7] Ibid. 140, 1384.
[8] Bull. U. S. Bureau Standards, 1, 349.

equivalent of silver. There is also a memoir by Reuterdahl[1] on electrochemical equivalents and atomic weights.

Makower[2] has attempted to determine, from their rates of diffusion, the molecular weights of the radium and thorium emanations. For the radium emanation he finds the values 85.5, 97, and 99, assuming the substance to be monatomic. The thorium emanation is but slightly different. Makower suggests that the emanation may fill the vacant place in the periodic table between molybdenum and ruthenium. The atomic weight of radium itself has been discussed by Jones,[3] who, from a critical examination of all the evidence, is inclined to favor the higher of the two rival values, namely, Ra = 258.

On the calculation of atomic weights, there is an interesting paper by J. Meyer.[4] An important suggestion by Luther[5] is to refer combining weights, through the aid of Faraday's law, to the C. G. S. system of units. In this way the question of standards might be settled, and a rational table devised.

FURTHER STUDIES ON THE HYDRATES OF SODIUM THIOSULPHATE.

By S. W. Young and W. E. Burke.

Received December 30, 1905.

Introduction.

In a previous paper[6] we gave an account of some investigations upon the solubility and composition of some of the hydrates of sodium thiosulphate. Since that time we have completed the study of the hydrates there mentioned, and also have discovered and investigated a number of new hydrates. This paper contains the results of this work, as well as a considerable number of observations upon the supercooling, superheating, and transitions of the various substances.

The various hydrates, their preparation and composition.

Following is a list of the hydrates of sodium thiosulphate, together with descriptions of the methods of their preparation,

[1] Trans. Amer. Electrochem. Soc. 7, 187.
[2] Phil. Mag. [9] 9, 56.
[3] Am. Ch. J. 34, 467.
[4] Z. anorg. Chem. 43, 242.
[5] Z. Elektrochem. 11, 273.
[6] This Journal, 26, 1413.

and later, experimental data regarding their composition. The classification and nomenclature used in this paper are based upon a definite system. This system cannot well be explained until after the experimental data have been considered. One point must however be made clear, namely, when, for example, a tetrahydrate is spoken of as "secondary" tetrahydrate, it does not follow that a primary, or any other tetrahydrate is known. The adjective is used simply to indicate certain affiliations of the hydrate, which will be explained later.

(1) Primary pentahydrate, formerly called α-pentahydrate. This is the ordinary commercial salt and is stable at all temperatures below 48.2°. It forms spontaneously from any of the other forms when they are cooled to about —35°, for in working with these other forms we had occasion to immerse sealed tubes containing them in liquid ammonia, and found that this treatment caused the formation of the primary pentahydrate in every case. So long as the tubes remained in the liquid ammonia no change could be observed, but as soon as they were taken out and warmed up, the primary pentahydrate would start and grow rapidly through the mass of crystals and solution contained in the tubes. The explanation of this is that the crystals start at the lower temperature, but grow extremely slowly. The rate of growth increases rapidly with the temperature and soon becomes very great. All the forms gave the same result, and a very brief immersion in the liquid ammonia was sufficient to start them over. The primary pentahydrate crystals belong to the monoclinic system.[1] We have not determined the crystalline structure of any of the other hydrates on account of the impossibility of handling them except in sealed tubes.

(2) Primary dihydrate (α-dihydrate), originally called *b*.[2] This is the stable form between 48° and 65°, and may be readily obtained by fusing the commercial salt and holding the fusion at a temperature of from 50–55° until crystallization starts. The crystals are coarse needles resembling those of the primary pentahydrate.

(3) Secondary pentahydrate, formerly called β-pentahydrate. For preparation see Young and Mitchell.[3] This form exists in

[1] Dammer: Handb. anorg. Chem. II, 2, 163.

[2] Young and Mitchell: This Journal, 26, 1391.

[3] Loc. cit.

long fine needles which, upon standing, undergo a peculiar slow transformation. The opaque mass of fine crystals gradually becomes clearer and in some cases perfectly transparent, to the eye resembling a very clear jelly. Its other properties remain unchanged. If partially melted and allowed to solidify, it comes down in fine needles, as at first.

(4) Secondary tetrahydrate, originally called *d*. Formed from secondary pentahydrate on heating to above 30°, the crystals resembling those of the pentahydrate very closely.

(5) Secondary monohydrate (α-monohydrate), formerly called *a*. Besides forming spontaneously in supercooled fusions of the pentahydrates,[1] it forms in solutions of anhydride at temperatures below 50°, and in solutions of the secondary tetrahydrate above about 41°. It grows very slowly even from concentrated solutions, the crystals being either long coarse needles, or small seemingly rectangular prisms, the habit depending on the conditions under which the crystallization occurs.

(6) Tertiary (acts also as quaternary) hexahydrate. This form was originally miscalled γ-pentahydrate and the method of its preparation is given under that name.[2] Prepared, as it usually was when first discovered, from fused pentahydrate, it came down as a white opaque mass. This mass is, of course, not pure hexahydrate but presumably a mixture of hexahydrate and anhydride. If prepared from a solution containing sufficient water, very hard transparent crystals are obtained.

(7) Tertiary sesquihydrate. This hydrate was discovered in a rather peculiar manner. In attempting to investigate the conduct of the mixture of hexahydrate and anhydride, formerly called γ-pentahydrate, in the neighborhood of the melting-point of the hexahydrate, some tubes containing this mixture were rotated in the thermostat, the temperature being raised only one-tenth of a degree at a time, and held at each temperature for two hours, it was noticed that at about 14.2° the mixture seemed to soften up a little. As it did not melt to more than a very slight degree with the gradual rise in temperature, some of the tubes were taken out and examined. The crystals found in the tubes were very fine needles, resembling those of the four-thirds-hydrate, but somewhat finer. Their rate of growth was much

[1] Young and Mitchell: Loc. cit.

[2] Ibid.

greater than that of the four-thirds-hydrate crystals, and they seemed to fill the mother-liquor even more completely.

(8) Tertiary monohydrate (β-monohydrate). This hydrate is formed from the tertiary sesquihydrate by transition at a little below 50°. The crystals resemble those of the secondary monohydrate.

(9) Quaternary four-thirds-hydrate ($3Na_2S_2O_3.4H_2O$) originally called *c*.[1] Besides forming from the hexahydrate on heating to about 15°, it sometimes forms spontaneously in supercooled solutions of anhydride. The crystals appear as fine needles, and if the solution is at all concentrated it becomes filled with them, and appears to be almost completely solidified, when in reality the crystals form but a small proportion of the total mass.

(10) Quintary dihydrate (β-dihydrate). This hydrate is formed from the four-thirds-hydrate by transition at temperatures slightly above 0°. Little is known about this transition, which was discovered in the following manner: Some tubes of the four-thirds-hydrate having been allowed to stand in ice-water for several days, it was found when they were taken out, that several had gone over into this new form. It crystallizes in very thin radiating plates, and is readily recognized when it first comes down. On standing, however, the plates thicken up and lose their distinctive character.

(11) Quintary monohydrate (γ-monohydrate). This hydrate is formed by heating the quintary dihydrate to temperatures above 35°. The crystals resemble those of the other monohydrates.

(12) Quintary hemihydrate. This is formed by heating the quintary monohydrate to temperatures above 50°. The crystals also resemble those of the monohydrates.

(13) Anhydride. The anhydride is very easily prepared as it is the stable form above 70°. The crystals appear to be rectangular prisms.

The composition of the different hydrates was determined in various ways, as was most convenient in the particular case. Following are the data concerning the composition, the hydrates being listed in the same order as above. For the determinations of the composition of the starred hydrates, see Young and Burke.[2]

[1] Young and Mitchell: Loc. cit.

[2] This Journal, 26, 1413.

(1) Primary pentahydrate, long known in the literature as a pentahydrate.

(2) Primary dihydrate.*

(3) Secondary pentahydrate.*

(4) Secondary tetrahydrate.* In addition to the direct determination of the composition of this hydrate, the fact that the solubility curve (see chart) meets the line of tetrahydrate composition at a right angle shows this substance to be a tetrahydrate.

(5) Secondary monohydrate.*

(6) Tertiary hexahydrate. The composition of this hydrate was determined in the following manner: A solution containing 59.4 per cent. of anhydride was prepared; tubes containing this solution were inoculated with crystals of the hexahydrate and when about one-half of the solution had crystallized, the composition of the remaining liquid was determined, and found to be the same as at the beginning. The crystals therefore had the same composition as the solution, whence the formula, $Na_2S_2O_3.6H_2O$.

(7) Tertiary sesquihydrate. The composition of this hydrate, and of all the succeeding ones, was determined in the following manner: Crystals of the desired modification were prepared in small glass tubes, about 7 mm. internal diameter and 10 cm. long, (Fig. 1, *a*); the major portion of the mother-liquor was removed from these tubes by placing the tips under water, and forcing in air through a fine glass tube. The constricted tip of the tube was then washed out with wet cotton, and heated in the flame until only a very small opening was left. This was necessary in order that the fine crystals should not be thrown out in the subsequent treatment. In order to guard against inoculation from floating particles, the brass cap *b* was placed over the open tip, being joined air-tight by means of the rubber band *c*. During the time that the caps and bands were not in use, they were kept under water, in order that they might not collect solid particles which would cause inoculation.

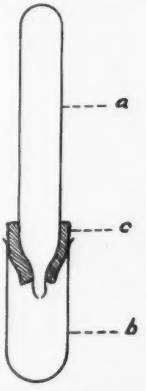


Fig. 1.

The tubes thus prepared were then placed in the holders of a

centrifugal machine and rotated for fifteen minutes. The machine gave 2500 revolutions per minute, and an effective radius of 6 inches. After centrifuging, the tubes were removed, weighed samples taken, and titrated with standard iodine solution.

To determine approximately the error introduced by the adhering mother-liquor, analyses were first made upon a known form, namely, the primary dihydrate. Following are the results obtained:

	Per cent. $Na_2S_2O_3$.		Per cent. of solution retained by crystals.
	Theoretical.	Found.	
(1)	81.43	77.76	13.90
(2)	81.43	78.50	11.10
(3)	81.43	77.91	13.30
			Average, 12.80

The large amount of solution retained by the crystals is due to the fact that small crystals were used, and to the very high viscosity of the solutions. In order to obtain comparative results, small crystals were always used, for while with some forms large crystals may be obtained, this is almost impossible with others. In making corrections it was assumed that the percentage of mother-liquor retained was always the same. The composition of the liquor was known in each case from solubility data.

Following are the results for the sesquihydrate: In this case as in all the following ones there is given under A the percentage of $Na_2S_2O_3$ found; under B this value as corrected from the data on primary dihydrate; under C the theoretical value corresponding to the given formula:

A.	B.	C.
81.60	84.90	....
82.37	85.70	85.41
82.21	85.60	....

(8) Tertiary monohydrate.

A.	B.	C.
86.48	89.40	89.80
86.32	89.30	....

(9) Quaternary four-thirds-hydrate.

A.	B.	C.
83.77	87.10	....
83.33	86.70	86.82
83.64	86.90	....

(10) Quintary dihydrate.

A.	B.	C.
80.11	82.80	....
80.24	82.90	81.43
80.26	82.90	....

These determinations are seen to be abnormally high in case of the quintary dihydrate. This may be due to either one of two reasons: (1) The substance may be a hydrate of the composition $5Na_2S_2O_3.9H_2O$, containing 82.99 per cent. of anhydride; (2) it may be that on account of the form of the crystals, less solution was retained than in the other cases. This hydrate crystallizes in large thin plates, which would be expected to retain less mother-liquor than the finer, needle-like crystals of the other hydrates. On the whole we are inclined to think that the substance is a dihydrate.

(11) Quintary monohydrate.

A.	B.	C.
85.41	88.70	89.80
86.24	89.50	....

(12) Quintary hemihydrate.

A.	B.	C.
91.22	94.80	94.62
91.49	95.10	....

(13) Anhydride.

A.	B.	C.
96.03	100.20	100.00
97.79	102.10	.....

Thus there are at present known thirteen crystalline forms of sodium thiosulphate, namely, one anhydride, one hemihydrate, three monohydrates, one four-thirds-hydrate, one sesquihydrate, two dihydrates, one tetrahydrate, two pentahydrates and one hexahydrate.

SOLUBILITY DETERMINATIONS.

Following are determinations of the solubility of the various hydrates mentioned in the previous paper[1] at temperatures not investigated at that time, also solubility determinations for the newer hydrates above mentioned. This work completes the data as to the solubility of all the known forms throughout their various ranges of existence, in so far as these ranges are included between the temperatures of 0° and 80°. Determinations were made at 5° intervals for all forms, except that in some cases

[1] Loc. cit.

determinations were made at smaller intervals, this being occasionally necessary in order to follow the course of the solubility curves more accurately.

(1) *The Method.*—In all essentials the method used was the one described in the previous paper. Several modifications of the details have, however, been introduced, and these will be described here.

(*a*) *The Thermostats.*—It was of course necessary to have thermostats which not only allowed of accurate and simple regulation, but which could also be readily changed from one temperature to another, over a wide range. For this purpose two well insulated copper tanks were prepared, and fitted with the usual gearing. The ordinary toluene regulator arranged for electrical contact was used. A supply of water from an external source was the thermal agent employed, hot water being used for the higher, and cold water for the lower temperatures. For higher temperatures the regulation was accomplished as follows: The regulator being set for the desired temperature, hot water from a tank was allowed to flow in through a thin rubber tube; this raises the temperature of the water in the thermostat until the mercury in the regulator makes contact with the adjustable platinum point, closing the circuit through two accumulators in parallel and an electromagnet; the armature of this electromagnet, on being pulled down, closes a stronger current through a second, more powerful electromagnet, so arranged that its armature in closing pinches the soft rubber tube, thereby shutting off the supply of hot water. As the temperature in the thermostat spontaneously falls, the contacts are again opened, and hot water is again admitted. For lower temperatures ice-water is used, and the contacts so arranged that when the circuit is closed in the first magnet, it is broken in the second. With this device it was a simple matter to work at any temperature between 0° and 95°, excepting that at 0° it was necessary to put crushed ice in the tanks. With two tanks of this sort, fairly rapid work was possible. The following details in the manipulation are of importance: (1) The circuit operating the first electromagnet should be of the lowest possible voltage to avoid excessive sparking at the contact in the regulator, which soils the mercury. A drop of water placed on the surface of the mercury, obviates to a great extent the bad effects of sparking; (2) the hot or cold water

should be introduced into the tank as close as possible to the bulb of the regulator, for thus the regulator will feel the temperature change too quickly rather than too slowly, which is favorable to accurate regulation; (3) the accuracy of regulation is increased by avoiding too great a difference of temperature between the water in the tank and the supply water. With this apparatus under favorable conditions, the fluctuations in temperature were so small as to be scarcely observable with a Beckmann thermometer.

(*b*) *Preparation of the Tubes.*—Originally the tubes were prepared by placing in them suitable amounts of water and thiosulphate, sealing them off and subjecting them to such roundabout treatment as would yield the desired form. With some of the forms this was very laborious, and the following method was devised: The requisite thiosulphate and water were put into the tube and the open end closed with a wad of wet cotton; the tubes were then heated in a water-bath until complete solution and sterilization were accomplished: they were then cooled, and crystals of the desired form introduced on the end of a wet glass rod, and finally the tip was sealed off. It was found that the cotton wad was ample protection against inoculation so long as it remained wet.

(*c*) *The Standard of the Iodine Solution.*—This was determined daily by the anhydrous sodium thiosulphate method.[1] Occasionally a check was made by running a solubility determination of the primary pentahydrate at some temperature at which the solubility had been previously accurately determined.

(*d*) *The Pipette.*—The pipette used is shown at *a* Fig. 2. It is easily made from an ordinary 1 or 2 cc. pipette, and possesses many advantages over the forms usually employed for such work. The sample is sucked up wholly into the bulb, and the weighing made by suspending the pipette in a horizontal position by means of the wire *b*. At lower temperatures, where the introduction of the hot, sterilized pipette might introduce con-

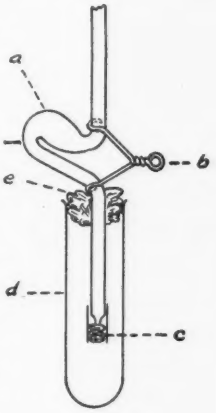


Fig. 2.

[1] Young: This Journal, **26**, 1028.

siderable errors, the tip of the pipette with its attached cotton-wool filter, *c*, was placed in a small test-tube, *d*, whose neck was packed with cotton-wool, *e*. After sterilization in an air-bath, it was removed and allowed to cool with the test-tube still attached. Kept in this condition it would remain sterile until needed.

(2) *Solubility Data.*—In the following determinations of solubility, two-tenths per cent. was taken as the maximum allowable variation between parallels. However in relatively few cases is the error much greater than one-tenth, and when required, as in cases where it was necessary to distinguish points on two very close-lying curves, it was found possible by taking special precautions, to reduce this error to considerably less than one-tenth.

TABLE I.—SOLUBILITY OF PRIMARY PENTAHYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 of solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
0°.....	33.35, 33.44	33.40	50.15
5°.....	35.34, 35.32	35.33	54.64
10°.....	37.36	37.37[1]	59.66
15°.....	39.09, 39.13	39.11	64.22

[1] For additional data at 10°, as well as data from 20° to 45°, see previous paper: Loc. cit. Melting-point is at 48.45°. Transition-point into primary dihydrate is at 48.17°.

TABLE II.—SOLUBILITY OF PRIMARY DIHYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 of solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
0°.....	52.68, 52.76, 52.76	52.73	111.60
5°.....	53.40, 53.46, 53.48	53.45	114.90
10°.....	53.95, 53.88, 53.98	53.94	117.10
15°.....	54.62, 54.62	54.62	120.40
35°.....58.16,	58.18, 58.21, 58.10, 58.11	58.15	139.00
40°.....	59.33, 59.32, 59.48	59.38	146.20
45°.....	60.71, 60.75	60.73	154.70
55°.....	63.83, 63.87	63.85	176.60
60°.....	65.66, 65.70	65.68	191.30
65°.....	68.03, 67.98, 68.10	68.04	212.90

For data at 20°, 25° and 30° see previous paper. Data at 35° taken in part from previous paper. New data at 40° C. substituted for that in the previous paper. Transition point into anhydride at 66.5°.

TABLE III.—SOLUBILITY OF SECONDARY PENTAHYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 of solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
0°.....	41.87, 42.06	41.96	72.30
5°.....	43.54, 43.59	43.56	77.17
10°.....	45.25, 45.25	45.25	82.65
15°.....	47.12, 47.27	47.19	89.36

For data from 20° to 30° see previous paper. Transition point into secondary tetrahydrate is at 30.22° C.

TABLE IV.—SOLUBILITY OF SECONDARY TETRAHYDRATE.

(See Table V in previous paper.) Transition point into secondary monohydrate at 40.65°. Melting-point at 41.65°.

TABLE V.—SOLUBILITY OF SECONDARY MONOHYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 of solution	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
0°	60.43, 60.46, 60.53	60.47	153.00
5°	60.75, 60.75, 60.73	60.74	154.70
10°	61.03, 61.06	61.04	156.70
15°	61.56, 61.51, 61.65	61.57	160.20
20°	62.03, 62.20, 62.10	62.11	163.90
25°	62.76, 62.71	62.73	168.30
30°	63.54, 63.53, 63.53, 63.63	63.56	174.40
35°	64.27, 64.30, 64.39	64.32	180.20
40°	65.16, 65.25, 65.25	65.22	187.60
45°	66.04, 66.07, 65.95	66.02	194.30
50°	66.79, 66.86	66.82	201.40
55°	67.86, 67.94	67.90	211.50

Data at 20°, 25° and 30° taken in part from previous paper. Transition point into anhydride at 56.5°.

TABLE VI.—SOLUBILITY OF TERTIARY (AND QUATERNARY) HEXAHYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 of solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
0°	46.12, 46.17	46.14	85.67
5°	48.41, 48.48	48.44	93.95
10°	51.63, 51.70	51.66	106.80
13°	54.92, 54.92, 54.98, 55.03	54.96	122.00

Melting-point at 14.35°. Transition point into the quaternary four-thirds-hydrate at 14.3°, and into tertiary sesquihydrate at 14.25° C.

TABLE VII.—SOLUBILITY OF TERTIARY SESQUIHYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 of solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
0°	57.40, 57.45	57.42	134.80
5°	57.80, 57.89	57.84	137.20
10°	58.26, 58.31	58.28	139.70
15°	58.79, 58.82	58.80	142.70
20°	59.27, 59.30	59.28	145.60
25°	60.17, 60.19	60.18	151.10
30°	60.77, 60.80	60.78	155.00
35°	61.53, 61.62	61.57	160.20
40°	62.53, 62.67	62.60	167.40
45°	63.97, 63.97, 63.98	63.97	177.50
47.5°	64.65, 64.71	64.68	183.10

Transition point into tertiary monohydrate at 48.5°.

TABLE VIII.—SOLUBILITY OF TERTIARY MONOHYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 of solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
47.5°	64.74, 64.83	64.78	183.90
50°	65.25, 65.28, 65.34, 65.35	65.30	188.20
52.5°	65.86, 65.92	65.89	193.20
55°	66.42, 66.46, 66.48	66.45	198.10
60°	68.05, 68.10	68.07	213.10

Transition point into anhydride at 61°.

TABLE IX.—SOLUBILITY OF THE QUATERNARY FOUR-THIRDS-HYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 of solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
0°	57.63, 57.64	57.63	136.00
5°	58.05, 58.11	58.08	138.60
10°	58.45, 58.45, 58.56	58.49	140.90
15°	58.98, 58.95, 59.00, 59.07	59.00	143.90
20°	59.54, 59.61	59.57	147.30
25°	60.30, 60.40	60.35	152.20
30°	60.98, 60.99, 61.06, 61.09	61.03	156.60
35°	61.90, 61.93, 61.95, 61.97	61.94	162.80
40°	62.91, 62.96, 62.98	62.95	169.90
45°	64.18, 64.26	64.22	179.50
50°	65.48, 65.42	65.45	189.50
55°	67.07, 67.08	67.07	203.70

Transition into anhydride at 58°.

TABLE X.—SOLUBILITY OF QUINTARY DIHYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 in solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
0°	57.61, 57.65	57.63	136.00
5°	58.20, 58.26	58.23	139.40
10°	59.02, 59.09	59.05	144.20
15°	60.01, 60.03	60.02	150.10
20°	61.02, 61.02	61.02	156.50
25°	62.27, 62.33	62.30	165.30
30°	63.54, 63.54, 63.56, 63.62	63.56	174.40
35°	65.27, 65.28	65.27	188.00

Transition point into quintary monohydrate at 27.5°.

TABLE XI.—SOLUBILITY OF QUINTARY MONOHYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 of solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
30°	63.30, 63.33, 63.39	63.34	172.80
35°	64.04, 64.10	64.07	178.40
40°	64.71, 64.76, 64.78	64.75	183.70
45°	65.55, 65.61	65.58	190.50
50°	66.53, 66.64, 66.56	66.58	199.20
55°	67.59	67.59	208.50

Transition point to quintary hemihydrate at 43°.

TABLE XII.—SOLUBILITY OF QUINTARY HEMIHYDRATE.

Temperature.	Parts $Na_2S_2O_3$ in 100 of solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
25°.....	64.21, 64.22	64.21	179.40
35°.....	64.59, 64.62	64.60	182.50
40°.....	64.95, 64.97, 65.04	64.99	185.60
45°.....	65.58, 65.61, 65.63	65.61	190.80
50°.....	65.94, 66.01, 66.07, 66.07	66.02	194.30
55°.....	66.55, 66.55, 66.61	66.57	199.10
60°.....	67.32, 67.48	67.40	206.70
65°.....	68.22, 68.26	68.24	214.90
70°.....	69.04, 69.08	69.06	223.20

Transition point into anhydride at 70°.

TABLE XIII.—SOLUBILITY OF ANHYDRIDE.

Temperature.	Parts $Na_2S_2O_3$ in 100 in solution.	Average.	Parts $Na_2S_2O_3$ in 100 of H_2O.
40°.....	67.38, 67.42	67.40	206.70
45°.....	67.57, 67.63	67.60	208.60
50°.....	67.75, 67.78	67.76	210.20
55°.....	68.14, 68.16	68.15	214.00
60°.....	68.45, 68.52	68.48	217.30
65°.....	68.77, 68.84	68.80	220.50
70°.....	69.04, 69.05, 69.07	69.05	223.10
75°.....	69.29, 69.42	69.35	226.30
80°.....	69.85, 69.87	69.86	231.80

DIRECT DETERMINATIONS OF TRANSITION POINTS.

In addition to locating transition points by the intersections of the various solubility curves, a number of these were also directly determined. This was necessary in cases where these points could not be readily located by means of the solubility curves, as for example is the case with melting-points, with very close-lying transition points, and with forms which refuse either to superheat or supercool.

(1) *The Method.*—Most of these determinations were made in the apparatus shown in Fig. 3. This consists of a containing vessel *a*. For this a 40×170 mm. test-tube was used.

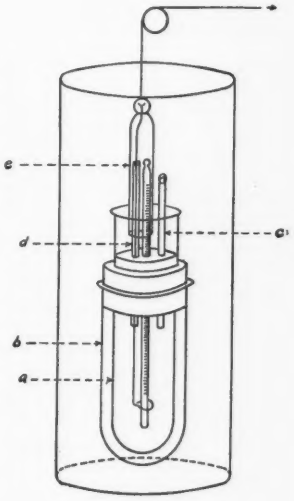


Fig. 3.

The lower part of this containing vessel was enclosed by the glass jacket *b*, into which it was fastened by means of a ring cut from A stout rubber stopper. The object of this outer air jacket was to prevent too rapid interchange of heat between the containing vessel and the surroundings. A rubber stopper was then chosen which closely fitted the bore of the containing vessel. Three holes were bored in this stopper, one of which carried the thermometer, a second carrying the short glass tube *c*. Into the third hole is introduced the glass tube *d*, through which plays the shank of the stout wire stirrer. In order that the apparatus might be operated without danger of inoculation from floating particles, the stirrer opening was protected by a water-seal. This consists simply of the glass tube *e*, into the top of which the end of the stirrer wire was sealed by means of sulphur. The glass tube *d* prevented any inflow of water through the stirrer opening. With the aid of this device a determination could be made with the apparatus completely submerged in an outer bath as shown in the figure.

The determinations were carried out in the following manner: A solution of the desired strength was placed in the containing vessel, the thermometer and stirrer placed in position, and the whole sterilized by submerging in a water-bath at a temperature of from 80° to 100°, the air jacket being removed to facilitate this operation. The apparatus was then allowed to cool, and the solution inoculated through the tube *c* with the hydrate whose transition it was desired to observe. During the crystallization the stirrer was kept in operation in order that the finest possible crystals should be obtained. The air jacket was then replaced, the apparatus immersed in the constant temperature bath and mechanical stirring begun. According to the direction of the transition, the bath was kept at about 1° above or below the expected transition temperature. When the thermometer in the apparatus showed about the same temperature as the one in the bath, the mixture was inoculated with the form into which transition was to occur, the stirring was continued and temperature readings were taken at regular intervals extending over a considerable range of time.

The thermometers used were two high-grade instruments, graduated into twentieth degrees. They were compared with normal thermometers calibrated by the Reichsanstalt, and their

readings found to coincide very closely. We believe that the following determinations are probably correct to within one-twentieth degree.

(2) *The Determinations.* (*a*) *The Transition Secondary Pentahydrate* $\rightleftarrows$ *Secondary Tetrahydrate.*—From the indications of the solubility curves this point was expected at slightly above 30°. The first determinations were made from below, *i. e.*, upon the transition of tetrahydrate into pentahydrate. The bath was held at 29°, thus supercooling the tetrahydrate by about 1°. Upon inoculation with pentahydrate the temperature rose very rapidly to 30.20°, and remained constant at that point for thirty minutes.

In order to determine this same transition point while the reverse reaction was going on, *i. e.*, while the pentahydrate was going over into tetrahydrate, the same apparatus still at 30.20° was used, the temperature of the bath being simply raised to 31.5°. The temperature of the mixture in *a* then rose slowly to 30.25°, and remained constant for forty-five minutes. The most probable value for this transition temperature is the average of these two readings, namely **30.22°**.

(*b*) *The Transition Primary Dihydrate* $\rightleftarrows$ *Secondary Tetrahydrate.*—From the solubility determinations this transition point was to be expected at about 31.5°. The bath was therefore held at 30°. The apparatus containing primary dihydrate and solution was placed in the bath and its temperature allowed to fall to 30.25°, *i. e.*, to a temperature just above that of the secondary pentahydrate-secondary tetrahydrate transition point, and inoculated with secondary pentahydrate. Since at this temperature the pentahydrate goes over into the tetrahydrate, this was equivalent to inoculation with the tetrahydrate itself, and much more convenient. Upon inoculation the temperature remained constant for about five minutes, and then very slowly rose to 31.45°, at which point it remained constant for one hour. A second determination made under the same conditions gave identical results. A third determination made with the bath at 31° gave as the transition point 31.48°.

As in the case of the previous transition, this transition point was also determined with the bath above the transition temperature. For this purpose the bath was held at 32°. Under these conditions the temperature rose from 31.48° (the tem-

perature reached with the bath below the transition temperature), to 31.55°, and remained constant for thirty minutes. The most probable value for this transition point is therefore **31.50°**.

Since the tetrahydrate readily superheats past its transition point into primary dihydrate, another method for the determination of this transition point is possible. This consists in the inoculation of the superheated tetrahydrate with crystals of the dihydrate. Several attempts were made to determine the point by this method. On account of the long, fibrous character of the tetrahydrate crystals it is impossible to stir a solution in which more than a small percentage of them is present. Thus, in carrying out these determinations the amount of transformable substance was very limited, and consequently the heat value per gram of mixture was very small. Add to this the fact that the reaction is very slow, and it is readily seen that the method is not a good one for obtaining accurate results. In all these determinations the bath was kept at 32°. In the first few attempts small quantities of primary dihydrate were used for inoculation. Under these conditions almost no temperature change was observed. When, however, about 5 cc. of a thick broth of the dihydrate crystals was added, a very gradual fall in temperature was noted. Two determinations gave respectively as the minimum temperatures, 31.70°, and 31.65°. These results, while interesting on account of the method in which they were obtained, were not considered of sufficient accuracy to be utilized in fixing the probable value of the transition point.

(*c*) *The Transition Secondary Pentahydrate* $\rightleftarrows$ *Primary Dihydrate.*—It was at first thought that this point could not be experimentally realized, as it was not supposed that the secondary pentahydrate could be superheated past its transition point into tetrahydrate. However, in one of the attempts to determine the primary dihydrate-secondary tetrahydrate point by inoculating the primary dihydrate with secondary pentahydrate as above described, it was noticed that the temperature rose, but soon became stationary at a point considerably below the one expected. The bath was at 31°, and the mixture before inoculation was at 29.75°. Upon inoculation the temperature rose rapidly to 30.52°, where it remained constant for twenty minutes. In another determination the bath was at 30°, and the mixture at 29°. Upon inoculation the temperature rose rapidly to 30.40°,

where it remained stationary for twenty-six minutes, after which it again rose slowly to 31.45°, thus giving an additional determination of the primary dihydrate-secondary tetrahydrate point. From these results it would seem largely a matter of chance whether upon inoculating primary dihydrate with secondary pentahydrate, the mixture proceeds directly to the higher point, or whether it stops either temporarily or permanently at the lower point. These results show the transition point between secondary pentahydrate and primary dihydrate to be at **30.46°**.

(*d*) *The Melting-point of Primary Pentahydrate.*—To determine this point a quantity of the pure primary pentahydrate was placed in the transition point apparatus, melted and sterilized, cooled to 35°, placed in a bath held at 47°, and then quickly inoculated with primary pentahydrate crystals. The temperature rose very rapidly from 35° to **48.45°**, where it remained constant for several minutes. That this temperature is the true melting-point of the primary pentahydrate, and not the temperature of its transition into primary dihydrate, is shown in the following paragraph.

(*e*) *The Transition Primary Pentahydrate⇄Primary Dihydrate.*—In the above experiment, after the temperature had remained constant for several minutes at 48.45°, it suddenly fell to 48.18°, where it again remained constant. After some time the temperature of the bath was raised 48.50°. This had no noticeable influence upon the temperature of the mixture, which remained constant at 48.18° for one hour. That this latter temperature was that of the transition primary pentahydrate-primary dihydrate can not be doubted. Still further evidence is, however, found in the results of the following experiment.

In this experiment a broth of the dihydrate crystals was brought to 42°, immersed in a bath held at 47°, and inoculated with the pentahydrate. The temperature rose rapidly to 48.17°, where it remained constant as long as observed. Thus the temperature of this transition is fixed at **48.17°**.

(*f*) *The Melting-point of Secondary Tetrahydrate.*—A solution of the composition of the tetrahydrate was prepared from weighed quantities of pentahydrate and anhydride, sterilized, brought to 33°, placed in a bath at 39°, and inoculated with secondary pentahydrate (see under *b*). The temperature rose with extreme rapidity to 41.65°, where it remained constant for a few minutes.

On attempting to repeat this determination, difficulty was invariably experienced, owing to the fact that during sterilization a crust of anhydride would form in the upper part of the apparatus. This was avoided by the following modification of the method: The materials in the requisite proportions, together with some mercury, were placed in a 100 cc. wide-mouthed bottle. The bottle was tightly stoppered and rotated in a thermostat at 80°. This rotation prevented the formation of the anhydride crust. The bottle was then taken out, cooled to 35°, after which the stopper was removed, the contents inoculated with secondary pentahydrate and a second sterile stopper, carrying the thermometer, quickly introduced. In order to avoid excessive radiation, the bottle was wrapped in a dry cloth. It was then violently shaken by hand, the mercury assisting the agitation, whereupon the temperature rose to 41.60°.

From a consideration of the results obtained by these two methods, the most probable value for this transition point is believed to be **41.65°**.

(*g*) *The Transition Secondary Tetrahydrate* $\rightleftarrows$ *Secondary Monohydrate.*—In both of the above determinations, after the temperature had remained for some time at the melting-point of the tetrahydrate, it fell, in the first case to 40.65°, in the second to 40.60°, at which points it remained constant for some time. Previous experience had shown that when the tetrahydrate undergoes transition with rising temperature, it is always the secondary monohydrate into which it is transformed. This, coupled with the evidence of the solubility curves, shows beyond doubt that the transition point there measured was that of the tetrahydrate into the secondary monohydrate. The most probable value for this point is **40.65°**.

(*h*) *The Melting-point of Tertiary (and Quaternary) Hexahydrate.*—This was determined by the second of the methods used with the tetrahydrate. Two determinations were made, the solution of the hexahydrate composition being cooled in each case to 10°. Upon inoculation the temperature rose in the one case to 14.35°, and in the other to 14.37°. As the room temperature was somewhat above that of the melting-point, it is considered that **14.35°** is the most probable value.

TABLE XIV.

Temperature.	Primary.		Secondary.		Tertiary.			Quinary.			
	Pentahydrate.	Dihydrate.	Pentahydrate.	Tetrahydrate.	Monohydrate.	Hexahydrate.	Sesquihydrate.	Monohydrate.	Quaternary four-thirds-hydrate.	Dihydrate.	Monohydrate.	Hemihydrate.	Anhydride.
0	33.40	52.73	41.95		60.47	46.14	57.42		57.63	57.63			
5	35.33	53.45	43.56		60.74	48.44	57.84		58.08	58.23			
10	37.37	53.94	45.25		61.04	51.66	58.28		58.49	59.05			
13	.....	.....	.....		.....	54.96	.....		.....	.....			
15	39.11	54.62	47.19		61.57		58.80		59.00	60.02			
20	41.20	55.15	49.38		62.11		59.28		59.57	61.02			
	M. P. at 48.45° C.												
	Tr. to primary dihydrate >48.17° C.												
		Tr. to anhydride >68.5° C.											
			Tr. to secondary tetrahydrate >30.22° C.										
25	43.15	56.03	52.15		62.73		60.18		60.35	62.30		64.21	
28	.....	.....	54.48		.....		.....		.....	.....		.....	
29.5	.....	.....	55.85		.....		.....		.....	.....		.....	
30	45.19	57.13	56.57		63.58		60.78		61.03	63.56	63.34	.....	
33.5	.....	.....		58.59	.....		.....		.....	.....	.....	.....	
35	47.71	58.18		.....	64.32		61.57		61.94	65.27	64.07	64.60	
36.2	.....	.....		60.51	.....		.....		.....	.....	.....	.....	
38.6	.....	.....		62.80	.....		.....		.....	.....	.....	.....	
40	50.83	59.38			65.22		62.60		62.95		64.75	64.99	67.40
45	55.33	60.73			66.02		63.97		64.22		65.58	65.61	67.60
47.5		.....			.....		64.68	64.78	.....		.....	.....	.....
50		62.28			66.82			65.30	65.45		66.58	66.02	67.76
52.5		.....			.....			65.89	.....		.....	.....	.....
55		63.85					66.45	67.07			67.59	66.57	68.15
60		65.68					68.07					67.40	68.48
65		68.04										68.24	68.80
70												69.06	69.05
80													69.35
													69.86
	Tr. to anhydride >61° C.					Tr. to tertiary sesquihydrate <48.5° C.							
						Tr. to quaternary four-thirds-hydrate >14.3° C.							
						M. P. at 14.35° C.							
							Tr. to tertiary monohydrate >48.5° C.						
								Tr. to anhydride >58° C.					
									Tr. to anhydride >70° C.				
										Tr. to quintary monohydrate >27.5° C.			
											Tr. to quintary hemihydrate >43° C.		
												Tr. to quintary monohydrate <43° C.	
													For transitions see later.
											Tr. to quintary dihydrate <27.5° C.		
										Tr. to secondary pentahydrate <30.22° C.			
									Tr. to secondary monohydrate >40.65° C.				
									M. P. at 41.65° C.				
									Tr. to quaternary four-thirds-hydrate >14.25° C.				
									Tr. to tertiary sesquihydrate >14.25° C.				

TABULAR AND GRAPHIC COMPILATION OF RESULTS.

The averages of all solubility determinations given above and in the previous paper, together with the temperatures of such transitions as spontaneously occur, are compiled in Table XIV. The symbol $>$ before a temperature indicates a transition with rising temperature, and the symbol $<$ a transition with falling temperature.

These results are also graphically plotted in Chart 1. The solid lines represent averages of actual determinations not more than 5° apart. The lines ------ are extrapolated. The lines —·—·—·— are lines of composition of certain of the hydrates. The curves as plotted follow the actual determinations within two tenths per cent. in all cases, and in the great majority of cases much more closely. Through a small error in draughting, the melting-point of the hexahydrate is placed about three-tenths of a degree too high. On the same chart the trio of transition points lying near 31° is also plotted on a much enlarged scale.

DISCUSSION OF THE RESULTS.

(1) *Supercooling.*—This phenomenon is of such common occurrence that only a few points of special interest will be taken up here. All of the hydrates of sodium thiosulphate supercool to a greater or less extent, at least when in contact with the saturated solution, this being the only condition under which we have worked with them. The range of temperature through which supercooling is possible varies greatly with the different hydrates, as does also the time for which they may remain supercooled. Thus, sealed tubes containing primary dihydrate have been kept at room temperature for nearly two years, and in no case has the primary pentahydrate appeared in them. Occasionally, however, the secondary pentahydrate has appeared in such tubes. On the other hand the tetrahydrate supercools to so slight a degree that no solubility determinations were possible at temperatures below its transition point into secondary pentahydrate. That slight supercooling does occur for a short time, is shown under *a*, p. 329.

On the whole our experience seems to indicate that possibly all supercooled systems are transitory, and that all such may, after the lapse of sufficient time (often very great), go over into the more stable systems.

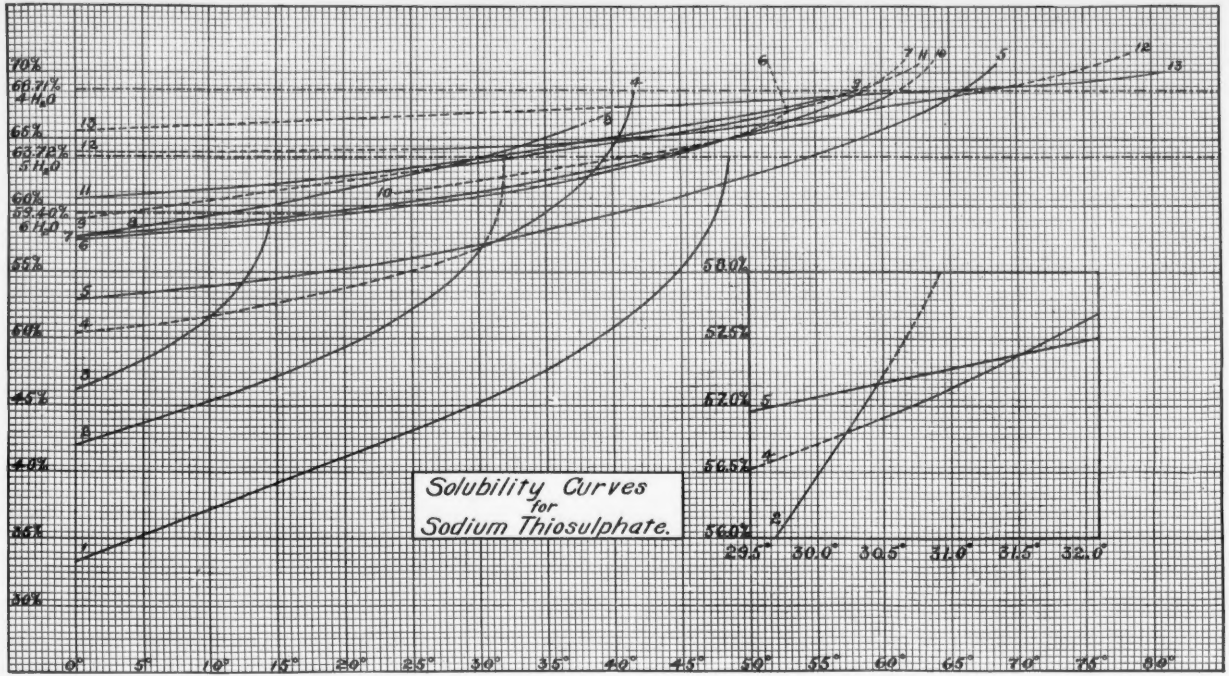


CHART I.—The curves are numbered at the lower ends, and where necessary, also at the upper ends. The compounds corresponding to this numbering are shown in the following tabulation: 1, Primary pentahydrate; 2, Secondary pentahydrate; 3, Tertiary (quaternary) hexahydrate; 4, Secondary tetrahydrate; 5, Primary dihydrate; 6, Tertiary sesquihydrate; 7, Quaternary four-thirds-hydrate; 8, Quintary dihydrate; 9, Quintary monohydrate; 10, Tertiary monohydrate; 11, Secondary monohydrate; 12, Quintary hemihydrate; 13, Anhydride.

(2) *Superheating.*—In the previous paper it was pointed out that the tetrahydrate offers a marked case of the supposedly very rare phenomenon of superheating. With the completion of the work on the hydrates of sodium thiosulphate, this phenomenon has been found to be of such common occurrence as to almost lead to the belief that it may be universal. A striking illustration of the frequency with which this phenomenon occurs may be seen from Chart 1, where it will be found that the solubility curves of seven different hydrates cross that of the hemihydrate in such a way that transitions into this latter would be expected. These transitions do not actually occur, with the single exception of that of the quintary monohydrate, and even this one does not occur until the temperature has been raised to fully 10° above the transition point.

In this connection the conduct of the secondary pentahydrate is of interest. For a long time this hydrate was not supposed to show superheating at all, but the determination of the temperature of its transition into primary dihydrate (see *c*, p. 330) shows that slight superheating does occur.

From considerable evidence which will be given later, it seems probable that the superheated state, like the supercooled, is, strictly speaking, transitory.

(3) *Origin of the New Phase in Transitions.*—A matter of very considerable interest in this field of work is the question as to whether, in the transition of one solid phase in contact with saturated solution into a second solid phase, the second solid phase appears as a product of the direct transformation of the first solid phase, or whether it may not have its origin directly in the homogeneous liquid. That the second solid phase is in many cases formed by the direct transformation of the first solid phase, cannot perhaps be reasonably doubted. However, evidence is at hand which proves conclusively that in some cases the second solid phase may have its origin solely in the homogeneous liquid phase. For example, clear crystals of primary pentahydrate on heating to 50° melt to a perfectly clear liquid, which condition persists for some minutes. Sooner or later, however, the liquid becomes turbid, owing to the appearance of crystals of the primary dihydrate. The same conduct is shown by the hexahydrate. In both of these cases the hydrates allowed themselves to be heated directly to their melting-points

and fused, without undergoing expected transitions, and the only possible source of the second solid phase was manifestly the homogeneous liquid. This conduct may at first seem surprising, but will, on second thought, be found wholly analogous to that of supercooled liquids from which, under certain conditions, a solid phase separates.

In the following discussion, this possibility in regard to the formation of the second solid phase in transitions with rising temperature, will be found of great utility, many curious phenomena finding therein a simple explanation. So commonly is this the case, that it almost seems as though the formation of the second solid phase directly from the first were the exception rather than the rule.

(4) *Classification and Nomenclature of the Hydrates.*—During the course of the investigation each hydrate was given a provisional name upon its discovery. This name indicated the composition of the hydrate, and in case of polymorphic forms being found, these were distinguished by Greek-letter prefixes, as for example, the α-, β-, and γ-monohydrates. This provisional nomenclature is adhered to in Chart 2, which shows the grouping since adopted. This grouping is based solely on the mutual transitions of the various hydrates. These transitions occur in such a way that the members of one group undergo transition into members of the same group and not into members of another group. For example take Group 2. The β-pentahydrate undergoes transition at 30.22° into the tetrahydrate. This undergoes no further transition until 40.65° is reached, when it goes into the α-monohydrate, which in turn at 56.5° goes into the anhydride. From Chart 1 it will be seen that this conduct involves superheating past five points on the part of the tetrahydrate, at any one of which points transition might ordinarily be expected. Similar conduct is shown by the hydrates constituting each of the other groups.

It will be noticed that with rising temperature, all of the groups yield anhydride, which therefore is a common member of all groups. The hexahydrate is also seen to occur in both the third and fourth groups. This is on account of the fact that this hydrate may undergo two spontaneous transitions, according to the temperature at which it is held (see 7, p. 317 and 9, p. 318). Beyond this none of the groups contain common members.

Perhaps these relationships may be more readily understood with the aid of a graphic representation. If we imagine each group existing in a plane of its own, the solubility curve of the anhydride being a line of intersection common to all of the five planes, we obtain the diagram shown in Fig. 4.

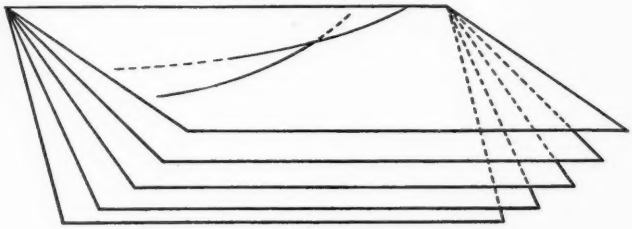
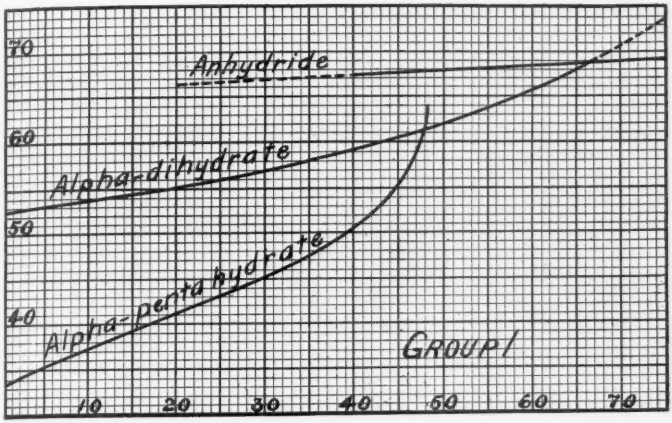


Fig. 4.

If we now imagine the solubility curves drawn in these planes, the curves for each group occupying a separate plane as indicated in the upper plane, we shall then have a fairly accurate representation of the conditions as they exist, the separation of the planes indicating the absence, under ordinary conditions, of direct transition between groups. Of course the hexahydrate curve will appear in two planes.

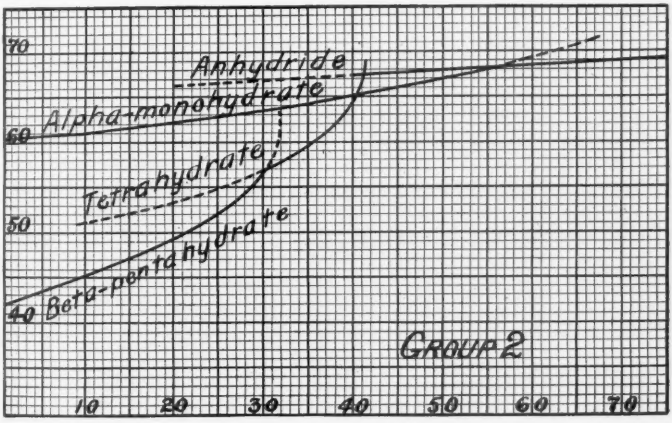
The nomenclature which has been adopted for these hydrates is based upon the above system of grouping. Those hydrates belonging to Group 1 are called primary hydrates, those belonging to Group 2 are called secondary, and those belonging to the third, fourth and fifth groups are called tertiary, quaternary and quintary, respectively. This system of nomenclature is adhered to in Chart 1. In the phraseology of the phase rule, a system including all the possible modifications of sodium thiosulphate and water would be spoken of as a "hylotropic system." The groups into which the system has been divided may therefore be called "hylotropic subsystems."

(5) *Characteristics of the Various Groups.* (*a*) *Group* 1.—This group having been so frequently used in the preceding paragraphs for the sake of illustration, little remains to be said. The primary pentahydrate undergoes transition into the primary dihydrate, but may be superheated past this transition temperature to that of the melting-point. Sooner or later the dihydrate appears in fusions kept near the melting-point. The



reverse transition of the supercooled dihydrate takes place only with great difficulty. With rising temperature the dihydrate goes into the anhydride.

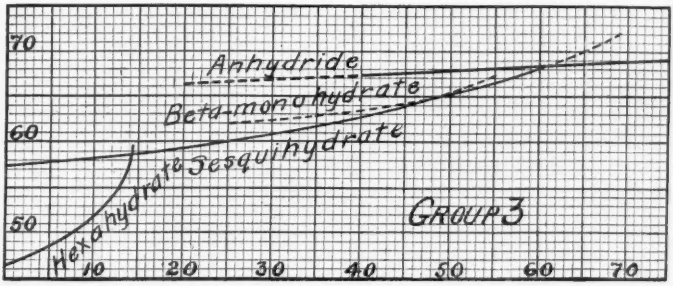
(*b*) *Group 2.*—The pentahydrate superheats only very slightly, going over with the greatest ease into the tetrahydrate. It is also impossible to supercool the tetrahydrate to any considerable



extent, since the reverse transition to pentahydrate occurs very readily. The transition of the tetrahydrate into the monohydrate takes place with greater difficulty, it being possible to

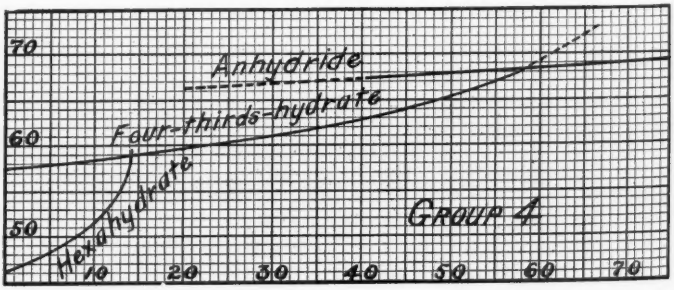
superheat the tetrahydrate to its melting-point for some minutes. The monohydrate supercools readily, only occasionally undergoing transition after months of standing at room temperature, and then not into the tetrahydrate, which is unstable at these temperatures, but into the pentahydrate (secondary). At higher temperatures the monohydrate goes into the anhydride.

(*c*) *Group 3.*—The hexahydrate acting as a tertiary hydrate may be superheated even to fusion without the appearance of the sesquihydrate. The converse supercooling is also very marked. The sesquihydrate appears when the hexahydrate is held for a



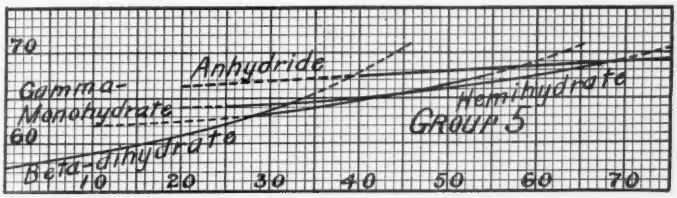
long time at temperatures but slightly above the corresponding transition point. The sesquihydrate goes over into the monohydrate at 48.50°, neither superheating nor supercooling occurring to any considerable extent. At higher temperatures the monohydrate goes over into anhydride.

(*d*) *Group 4.*—The quaternary group of hydrates conducts itself very similarly to the tertiary. The hexahydrate superheats to fusion, but if the fusion is held for some time at tem-



peratures a degree or two above the melting-point, the four-thirds-hydrate appears, especially if anhydride is present. At a higher temperature the four-thirds-hydrate goes over into anhydride.

(*e*) *Group 5.*—The quintary group is in some respects the most interesting of all. In the first place the dihydrate superheats not only past the monohydrate, but also past the hemihydrate. When the limit of superheating is reached, the transition takes place, not into the hemihydrate, as might be expected, but directly into the monohydrate, that is, into that form with respect to which it is most superheated. The monohydrate super-



cools but slightly with respect to the dihydrate. On the other hand, the monohydrate readily superheats some 10° above the transition point into hemihydrate, where a limit to its persistence in the superheated state is found, and it goes over into the hemihydrate. The hemihydrate readily supercools with respect to the monohydrate, and also with respect to the superheated dihydrate. At 70° the hemihydrate goes over into the anhydride.

(6) *Inter-group Connection.*—From what has already been said, the possibilities for inter-group connection should be reasonably clear. These possibilities may, however, be briefly summarized here. In the first place, the anhydride, being a member common to all groups, might naturally be looked to as a source of other members of each group, merely by reverse transition. It has been found experimentally that the anhydride, on cooling to below 40°, sooner or later invariably yields the secondary monohydrate. However, while making the solubility determinations of the anhydride between 45° and 55°, values which lay upon the curve of the four-thirds-hydrate were frequently obtained, thus showing transition into the quaternary group. It is not unreasonable to assume that, under the proper conditions, transitions of the anhydride into members of the other groups might occur.

The hexahydrate, as has been repeatedly indicated, serves to connect the tertiary and quaternary groups. The transition of the quaternary four-thirds-hydrate into the quintary dihydrate, which is complete at 0° within four or five days, gives connection between these groups. In general supercooled hydrates not infrequently undergo transition into members of other groups. Thus both the four-thirds-hydrate and the primary dihydrate, upon long standing at room temperature, have been observed to yield secondary pentahydrate. Analogously, superheated hydrates, particularly if held at temperatures below that of their usual group transition points, may yield hydrates belonging to other groups. Thus tubes containing quintary dihydrate, and in which this form had persisted for some weeks, occasionally went over into the four-thirds-hydrate. The opportunities for such transitions are very numerous. For example, solutions in which hexahydrate crystals are present, if held at a temperature just below that of the transition into the sesquihydrate, might yield primary dihydrate after sufficient time. Several such possibilities exist in the case of the tetrahydrate.

Besides the above methods of passing from one group to another, there is also the possibility of obtaining members of different groups from solutions which contain no crystalline hydrate whatever. Thus solutions of about pentahydrate composition on cooling to between 10° and 20° below zero, sometimes yield secondary pentahydrate, and sometimes hexahydrate, while on cooling to about 35° below zero they yield primary pentahydrate.

(7) *Analogies between Supercooling and Superheating.*—A careful consideration of the experimental evidence given in this paper, together with the intimate familiarity with these phenomena which we have gained through working for a considerable period of time in this field, have led us, in so far as generalizations may be drawn from work upon a single hylotropic system, to the following conclusions concerning the phenomena of supercooling and superheating.

(*a*) *That Supercooling and Superheating are Probably of Invariable Occurrence when a System Passes through a Transition Point.*—(Melting-points are to be considered as excluded from this discussion.) On Chart 1 there are to be found 29 intersections of solubility curves, each one of which locates a transition

point. Solubility determinations show that marked supercooling occurs in respect to 24 of these points. Other evidence shows that slight supercooling occurs in respect to 3 others. Concerning the remaining 2, no positive evidence is at hand.

Solubility and melting-point determinations also prove conclusively that superheating occurs in respect to 22 of the 29 points. Five of the remaining points are those at which transition into the anhydride occurs. In regard to these and one of the other points, there is evidence of slight superheating. In the three cases in which either supercooling or superheating has not been definitely found, there is no evidence whatever to show that these phenomena do not occur.

(*b*) *That the Two Phenomena are Subject to Essentially the Same Laws.*—The transformation of a supercooled system into a more stable one has been found by several investigators to be determined mainly by two factors: First, the degree of supercooling, by which is meant the extent to which the system is cooled below its transition point; in heterogeneous systems, such as those with which we have to deal here, the concentration factor may be eliminated, as the concentration is wholly determined by the temperature. Second, the time during which the system is held at a given temperature. Thus the phases of a more stable system, if they do not appear in a metastable system at a given temperature after a short time, may appear after a longer time. The transformations of superheated systems into more stable ones are controlled by the same conditions. For example, the quintary dihydrate, whose transition point into the quintary monohydrate lies at about 27.5°, remains in the superheated state for a long time at 30°, and at 35° remains in this condition long enough for accurate determinations of its solubility to be made, although at this latter temperature transition not infrequently occurs within an hour. At 40° the transition begins so soon that no solubility determinations could be obtained. In so far as they have been investigated, other cases show the same conduct.

Almost the only distinction between the two phenomena lies in the fact that the degree of supercooling possible, as well as the time during which a system may be held in the supercooled state, are usually greater than the corresponding possibilities in the case of superheating. However, reference to Chart 1

shows several cases for which this is not true, as for example, the transition between the monohydrate and the dihydrate of Group 5. The fact that, at least with all substances having positive temperature coefficients of solubility, superheating involves an increase in the total concentration, while supercooling involves a decrease in this value, may possibly explain why supercooling so often takes place to a greater degree than does superheating.

(8) *Application of the Nuclear Hypothesis.*—In a previous paper[1] an hypothesis was suggested to explain certain phenomena in regard to supercooling. Since experience had clearly shown that solutions and fusions obtained from the different hydrates of sodium thiosulphate conducted themselves in very different ways upon supercooling, the assumption was made that these solutions and fusions contained nuclei whose nature depended upon that of the hydrate used in their preparation. It was assumed that the character of the hydrate which would appear in a given supercooled solution or fusion, depended upon the character of the nuclei contained in it. For details, reference must be made to the original. This hypothesis has been of great assistance in the present further researches, and an explanation of the above results will now be given from this point of view.

(*a*) *Superheating.*—In the same way that this hypothesis has already been applied to supercooling, it may also be applied to superheating. Thus when a hydrate is superheated past a transition point, the expected transition will occur if the requisite nuclei are present in the solution, after sufficient time has elapsed for the nuclei to form the necessary crystalline aggregate. This, of course, presupposes that the second solid phase has its origin in the solution, which is known to be true in all cases where evidence has been obtained. The time required for the nuclei to form a crystalline aggregate may be very different in different cases, which accounts for the fact that different forms show very different degrees of superheating.

(*b*) If it be assumed that the nuclei are formed as a result of slow reaction of some sort in the solution, the fact that this reaction would undoubtedly be accelerated by increase of temperature would account for the fact that less superheating than supercooling is possible, other things being equal.

[1] Young and Mitchell: Loc. cit.

(*c*) *The Nuclear Explanation of Grouping.*—The fact upon which the division of the hydrates into groups rests, is that a given hydrate can superheat past points at which, from consideration of the energy relationships, transition could occur, but that each such hydrate selects a certain specific other hydrate into which it becomes transformed. A group then consists of such hydrates as are regularly formed from a given initial hydrate by transitions with rising temperature. If the principle that the new solid phase has its origin in the liquid phase is accepted, there seems to be no simple explanation of this conduct on the basis of the usual conception that the solutions formed from different solid phases of the same system are identical. On the other hand, the nuclear hypothesis offers a very simple explanation. If a given hydrate in contact with saturated solution be superheated past a number of transition points, that particular transition will occur for which the nuclear condition of the solution is most favorable. If this particular transition be excluded, as, for example, by holding the temperature below that of the corresponding transition point, that one of the remaining possible transitions, for which the nuclear condition of the solution is most favorable, will occur. In case the nuclear condition of the solution is relatively unfavorable for the occurrence of any of the possible transitions, a very long time may elapse before any transition whatever will be realized. From this it will be seen that, if the requisite conditions be maintained for a sufficient length of time, any possible transition might be realized. From these considerations, which are based upon direct experimental evidence, the belief that both the supercooled and the superheated states are always transitory, would seem to find reasonable justification, it being borne in mind that a transitory state may persist for a long time.

From this point of view, the grouping of the hydrates, as given above, is seen to represent nothing more nor less than the conduct of the hydrates with rising temperature, under the usual laboratory conditions, where a considerable range of temperature is compassed in a relatively short time. If conditions were such that a very much more gradual rise in temperature was used, an entirely different grouping would probably be found. With falling temperature the grouping is usually the same as with rising temperature, although exceptions to this occur.

(*d*) *The Ostwald Rule.*—The rule suggested by Ostwald, that when a supercooled system undergoes transition, it is always into the next lying, that is, the most metastable of all the possible systems, is so frequently violated by the hydrates of sodium thiosulphate that, at least in this system, it cannot be considered as even approximately representing the facts. The same is true for superheated systems. For example, quintary dihydrate, superheated to 40°, undergoes direct transition into the quintary monohydrate, thereby passing two forms metastable to the monohydrate, either of which, when once produced, persists at this temperature, and even at temperatures much below this, for a long time. Other similar cases may be found by reference to Chart 1. The explanation of this by the nuclear hypothesis is self-evident.

SUMMARY.

The results of the foregoing investigation may be summarized as follows:

(1) Thirteen crystalline modifications of sodium thiosulphate are described, namely, one hexahydrate, two pentahydrates, one tetrahydrate, two dihydrates, one sesquihydrate, one four-thirds-hydrate, three monohydrates, one hemihydrate, and one anhydride.

(2) Data proving the composition of these hydrates are given.

(3) The solubility of the various forms has been determined at intervals of 5° or less over the range of temperature extending from zero to 80°.

(4) All of the transition points of the system have been determined from the intersections of the solubility curves, and a considerable number have been also directly measured.

(5) Numerous observations concerning the supercooling and superheating of the different forms are recorded. Evidence is cited which tends to show that, in so far as this hylotropic system is concerned, superheating is as common as supercooling, in fact that both probably occur in the neighborhood of every transition point, excluding melting-points. Evidence is also given which seems to indicate that both phenomena are probably transitory.

(6) It has been found possible to divide the hydrates of this system into groups, on the basis of their conduct in undergoing

transition with rising temperature. In this connection many cases are cited which conflict with the Ostwald rule.

(7) The nuclear hypothesis has been shown to afford a simple explanation of the phenomena described.

STANFORD UNIVERSITY, CAL., December 1905.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

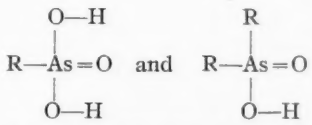
ARSONIC AND ARSINIC ACIDS.

BY WILLIAM M. DEHN AND S. J. MCGRATH.

Received January 2, 1906.

ARSONIC acids may be considered as derived from arsenic acid, $AsO(OH)_3$, by replacing one of the hydroxyl groups by a univalent hydrocarbon or substituted hydrocarbon radicle; thus the arsonic acids have the general formula $R—AsO(OH)_2$. Arsinic acids may be considered dialkyl or dialphyl substitution-products of arsenic acid and have the general formula RR′AsOOH, wherein R and R′ are any two univalent hydrocarbon radicles. All of the arsinic acids hitherto prepared have the two radicles identical, except phenyl-*p*-toluylcacodylic acid.[1] The arsinic acids are, of course, homologues of cacodylic acid and are therefore frequently termed cacodylic acids—for instance phenylarsinic acid is also known as phenylcacodylic acid.

The structural formulas usually assigned to the arsonic and arsinic acids are:



The best proof of the direct union[2] of the radicles with arsenic is seen in their reduction to the corresponding arsines,[3] which unquestionably contain the radicles in direct union with arsenic:

$$RAsO_3H_2 + 6H = RAsH_2 + 3H_2O$$

$$R_2AsOOH + 4H = R_2AsH + 2H_2O.$$

The possibility here of molecular rearrangement is precluded

[1] Ann. 321, 157.

[2] Ibid. 107, 269.

[3] Ber. 27, 1378; Am. Ch. J. 33, 104.

by the fact that the arsines spontaneously reoxidize to the respective acids:[1]

$$RAsH_2 + 3O = RAsO(OH)_2$$
$$R_2AsH + 2O = R_2AsOOH.$$

Proof of the pentavalent condition of the arsenic atoms in the arsonic and arsinic acids is seen in their stability towards oxidizing agents, as for instance toward nitric acid[2] or the halogens.[3] Whereas all soluble arsenic compounds that are known to contain trivalent arsenic easily reduce nitric acid and decolorize bromine water, the arsonic acids and the arsinic acids are indifferent toward these reagents, therefore their arsenic atoms must be held in the pentavalent condition.

The remainder of the structure of the arsonic acids and the arsinic acids is established by their basicity. The arsonic acids are dibasic,[4] and the arsinic acids are monobasic; the former possess two hydroxyls and the latter, only one. All of the facts are therefore in accordance with the above-mentioned structural formulas.

According to some recent work of Hantzsch,[5] however, conductivity measurements of methylarsinic acid (cacodylic acid) tend to show that when treated with an excess of caustic alkali, it does not react strictly as a monobasic acid, but, at least in part, as the sodium salt of a tribasic acid. His data are as follows:

			$(CH_3)_2AsO_2Na + NaOH$.		
	$(CH_3)_2AsO_2Na$.	NaOH.	By addition.	Found.	Difference.
M_1.....	56.8	202.0	258.0	232.8	25.2
M_2.....	56.8	201.9	257.9	233.1	24.8

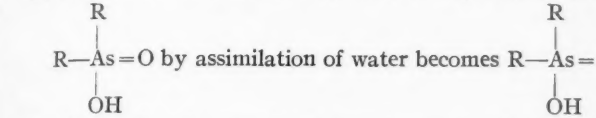
Hantzsch concluded that in the presence of one molecule of sodium hydroxide, cacodylic acid functionates as a monobasic acid,

$$(CH_3)_2AsO_2H + NaOH = (CH_3)_2AsO_2Na + H_2O,$$

but in the presence of an excess of sodium hydroxide it forms the molecular aggregate $(CH_3)_2As(OH)(ONa)_2$, and thus cacodylic acid functionates also in the tribasic form $(CH_3)_2As(OH)_3$. This effect is very slight, however, and disappears entirely in N/48 solution.

[1] Am. Ch. J. **33**, 123; **35**, 9.
[2] Ann. **46**, 9; Ibid. **208**, 3, 32.
[3] Ibid. **201**, 231.
[4] Ibid. **107**, 290; **320**, 277.
[5] Ber. **37**, 1076.

This evidence is not at variance with, but is in confirmation of, the above-mentioned structural formula, that is, the formula



the former bearing to the latter the same relation that metaphosphoric acid does to orthophosphoric acid.

Methods of Preparation.—There is available at present only one good general method for the preparation of both arsonic and arsinic acids; *viz.*, the hydrolysis of the corresponding radicle-halogen compounds:

$$RAsCl_4 + 3H_2O = RAsO(OH)_2 + 4HCl$$
$$R_2AsCl_3 + 2H_2O = R_2AsOOH + 3HCl.$$

The first application of this general reaction was made by Baeyer in the preparation of cacodylic acid:[1]

$$(CH_3)_2AsCl_3 + 2H_2O = (CH_3)_2AsOOH + 3HCl.$$

The first application in the aromatic series was made by La-Coste and Michaelis[2] in the preparation of phenylarsonic acid:

$$C_6H_5AsCl_4 + 3H_2O = C_6H_5AsO(OH)_2 + 4HCl.$$

Modifications of the above general method are found in the oxidation of monomethylarsine dichloride by means of moist silver oxide,[3]

$$(CH_3)AsCl_2 + 2Ag_2O + H_2O = (CH_3)AsO(OH)_2 + 2AgCl + 2Ag;$$

the oxidation of *m*-xylylarsine dichloride by means of hydrogen peroxide,[4]

$$(C_8H_9)AsCl_2 + 2H_2O_2 = (C_8H_9)AsO(OH)_2 + 2HCl + O;$$

and the oxidation of primary[5] and secondary[6] arsines by atmospheric oxygen, etc.,

$$RAsH_2 + 3O = RAsO(OH)_2,$$
$$R_2AsH + 2O = RAsOOH.$$

The intermediate compounds in the preparation of arsonic and arsinic acids, *viz.*, the trivalent radicle-halogen compounds, are derived by two general reactions:

[1] Ann. 107, 268.
[2] Ibid. 201, 202.
[3] Ibid. 107, 268.
[4] Ibid. 320, 333.
[5] Ber. 34, 3594; Am. Ch. J. 33, 124.
[6] Ber. 27, 1378; Am. Ch. J. 35, 9.

(1) The interaction of arsenic trihalides with mercury alkyl or mercury alphyl:

$$HgR_2 + 2AsCl_3 = HgCl_2 + 2RAsCl_2$$
$$HgR_2 + AsCl_3 = HgCl_2 + R_2AsCl.$$

(2) The condensation of arsenic trihalides and alkyl or alphyl monohalides by means of sodium:

$$RCl + AsCl_3 + 2Na = RAsCl_2 + 2NaCl$$
$$2RCl + AsCl_3 + 4Na = R_2AsCl + 4NaCl.$$

The first application of reaction (1) to the aromatic arsenic compounds was made by LaCoste and Michaelis[1] in the preparation of phenylarsine dichloride:

$$(C_6H_5)_2Hg + 2AsCl_3 = 2(C_6H_5)AsCl_2 + HgCl_2.$$

The first in the fatty series was made by LaCoste[2] in the preparation of ethylarsine dichloride:

$$(C_2H_5)_2Hg + 1AsCl_3 = C_2H_5AsCl_2 + C_2H_5HgCl.$$

The first application of reaction (2) to the aromatic series was made by Michaelis and Rees[3] in the preparation of triphenylarsine and its subsequent transformation to phenylarsine dichloride on heating with an excess of arsenic trichloride:

$$3C_6H_5Cl + AsCl_3 + 6Na = (C_6H_5)_3As + 6NaCl$$
$$(C_6H_5)_3As + 2AsCl_3 = 3(C_6H_5)AsCl_2.$$

The first application of reaction (2) to the fatty series was made by Dehn and Wilcox[4] in the preparation of mono- and diisoamylarsine chlorides:

$$C_5H_{11}Cl + AsCl_3 + 2Na = C_5H_{11}AsCl_2 + 2NaCl$$
$$2C_5H_{11}Cl + AsCl_3 + 4Na = (C_5H_{11})_2AsCl + 4NaCl.$$

Besides the above general methods for the preparation of arsonic and arsinic acids there are a number of special methods which are of great importance.

(1) The reaction of alkyl halides with alkali arsenites to form fatty arsonic acids:

$$As(ONa)_3 + RI = RAsO(ONa)_2 + NaI.$$

This reaction was first employed by Meyer,[5] was modified by Klinger and Kreutz[6] and was elaborated and extended by Dehn.[7]

[1] Ann. 201, 196.
[2] Ibid. 208, 33.
[3] Ber. 15, 2876.
[4] Am. Ch. J. 35, 48.
[5] Ber. 16, 1440.
[6] Ann. 249, 247.
[7] Am. Ch. J. 33, 131.

(2) The preparation of cacodylic oxide by heating potassium acetate and arsenic trioxide:

$$4CH_3CH_2OK + As_2O_3 = ((CH_3)_2As)_2O + 2CO_2 + 2K_2CO_3,$$

and its oxidation to cacodylic acid:

$$((CH_3)_2As)_2O + H_2O + 2O = 2(CH_3)_2AsOOH.$$

This reaction has not, however, yielded a single homologue of cacodylic acid.

The arsonic acids hitherto known and studied are as follows:

1. Methyl.[1]
2. Ethyl.[2]
3. Phenyl.[3]
4. Nitrophenyl.[4]
5. Dimethylaminophenyl.[5]
6. *p*-Anisyl.[6]
7. *p*-Phenetyl.[7]
8. *p*-Benz.[8]
9. *m*-Benz.[9]
10. Nitrobenz.[10]
11. *o*-Toluyl.[11]
12. *m*-Toluyl.[12]
13. *p*-Toluyl.[13]
14. Nitrotoluyl.[14]
15. Tertiary butylphenyl.[15]
16. *o*-Dimethylamino-*p*-tolyl.[10]
17. *m*-Xylyl.[16]
18. *p*-Xylyl.[17]
19. Monochlorxylyl.[18]
20. Dichlorxylyl.[18]
21. Nitroxylyl.[18]
22. *m*-Tolu.[19]
23. *p*-Tolu.[20]
24. Phthalo.[19]
25. Pseudocumyl.[21]
26. *p*-Cumyl.[21]
27. *α*-naphthyl.[22]
28. *β*-naphthyl.[23]

It will be seen that though some twenty-six arsonic acids of the aromatic series have been prepared only two of the fatty series have been prepared. We herein contribute two new fatty arsonic acids; *viz.*:

29. Propyl. 30. Isoamyl.

Also the aromatic arsonic acid,

31. Benzyl.

The arsinic acids hitherto prepared and studied are the following:

[1] Ber. 16, 1440; Ann. 107, 263; 249, 149.
[2] Ann. 208, 34; Am. Ch. J. 33, 132.
[3] Ibid. 201, 203.
[4] Ber. 27, 265.
[5] Ann. 270, 139.
[6] Ber. 20, 51.
[7] Ann. 320, 300.
[8] Ibid. 208, 5.
Ibid. 320, 329.
[10] Ibid. 320, 325.
[11] Ibid. 201, 255.
[12] Ibid. 320, 328.
[13] Ibid. 201, 255.
[14] Ibid. 320, 321.
[15] Ibid. 320, 342.
[16] Ibid. 320, 333.
[17] Ibid. 320, 338.
[18] Ibid. 320, 334.
[19] Ibid. 320, 335.
[20] Ibid. 320, 339.
[21] Ibid. 320, 340.
[22] Ber. 11, 1503.
[23] Ann. 320, 344.

1. Methyl.[1]
2. Ethyl.[2]
3. Phenyl.[3]
4. Benzyl.[4]
5. *p*-Toluyl.[5]
6. Nitrophenyl.[6]
7. Benz.[7]
8. Phenyl-*p*-toluyl.[8]
9. Isoamyl.[9]

Normal Propylarsonic Acid.—This acid was prepared in the same manner as ethylarsonic acid.[10] To 275 grams of arsenic trioxide (1 mol.) and 460 grams of potassium hydroxide (6 mols.), sufficient water was added to cause complete solution. After cooling, alcohol was added to the point of incipient precipitation of potassium arsenite; then 460 grams of normal propyl iodide (2 mols.) were added and the mixture was shaken. Usually either some potassium arsenite or some propyl iodide precipitates at this stage, but a homogeneous solution may be produced by adding either water or alcohol; or, when the solution is too concentrated, both must be added. After keeping the mixture in tightly-stoppered bottles for a number of days, the following reaction:

$$As(OK)_3 + C_3H_7I = (C_3H_7)AsO(OK)_2 + KI,$$

and the unavoidable side-reaction:

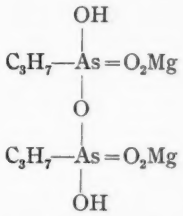
$$C_2H_5OK + C_3H_7I = C_2H_5—O—C_3H_7 + KI,$$

were complete. The mixture was then subjected to distillation, to remove the alcohol and the ethylpropyl ether. Hydrochloric acid was added to the point of incipient precipitation; then a stream of chlorine was passed in until the pure white double salt[11] first formed was dissolved and all of the iodine was precipitated. The filtrate was treated in the cold with magnesium mixture to precipitate the arsenate; upon boiling the filtrate from the ammonium magnesium arsenate, with more magnesium mixture, the *magnesium salt of normal propylarsonic acid* was precipitated as pearly-white, soapy crystals. Yield, 42 per cent. The magnesium salt was dried and analyzed:

	Per cent. Mg.
Salt dried at 100°–105° for eight hours	11.93
Salt dried at 130°–140° for six hours	11.99
Salt dried at 135°–160° for four hours	12.09
Salt dried at 190°–200° for five hours	13.38
Theory for $(C_3H_7AsO_3Mg)_2H_2O$	12.05
Theory for $C_3H_7AsO_3Mg$	12.48

[1] Ann. **46**, 2.
[2] Ibid. **92**, 365.
[3] Ibid. **201**, 231; **321**, 150.
[4] Ibid. **233**, 82.
[5] Ibid. **208**, 20.
[6] Ibid. **208**, 25.
[7] Ibid. **321**, 151.
[8] Ibid. **321**, 157.
[9] Am. Ch. J. **35**, 52.
[10] Ibid. **33**, 132.
[11] Ibid. **33**, 141.

These analyses indicate that the magnesium propylarsonate, like magnesium ammonium arsenate[1] dried above 100°, contains one molecule of water of crystallization to two molecules of the anhydrous salt. Drying above 190° not only removed this water of crystallization from magnesium propylarsonate but also partially decomposed the salt. Its probable structural formula is:



Free n-propylarsonic acid was prepared by treating the magnesium salt in the cold with the calculated quantity of concentrated sulphuric acid and then extracting with alcohol. Upon evaporating the alcoholic solution the acid was obtained as needle-form crystals.

The acid is very soluble in water; 100 parts of an aqueous solution at 26° contained 43 parts of acid. It is also very soluble in alcohol but is insoluble in ether.

n-Propylarsine Disulphide.—A quantity of the magnesium propylarsonate was dissolved in dilute hydrochloric acid and treated with hydrogen sulphide. A heavy, light yellow oil was slowly precipitated. It was extracted with carbon bisulphide, dried with calcium chloride and freed from the solvent by evaporation. The analysis gave 35.29 per cent. of S. Calculated for $C_3H_7AsS_2$, 35.16 per cent.

Therefore the reaction was:

$$C_3H_7AsO(OH)_2 + 2H_2S = C_3H_7AsS_2 + 3H_2O.$$

The density of the disulphide was found to be 1.8. It is a viscid oil that becomes a gummy mass below —10°.

Isoamylarsonic Acid.—This acid was prepared in a manner nearly identical with the manner of preparation of the *n*-propylarsonic acid. One molecule of arsenic trioxide (150 grams) was dissolved in six molecules of potassium hydroxide (254 grams) and treated with two molecules of isoamyl iodide (300 grams).

[1] Z. anal. Chem. 10, 62.

The reaction mixture was permitted to stand for two or three days, when the alcohol was removed by distillation; the solution was then *carefully* neutralized and filtered from the double salt of $As_2O_3.2KI$. Upon acidifying, a mass of shining scale-like crystals separated, usually after some time; they were filtered off, washed, recrystallized, dried and analyzed. Calculated for $C_5H_{11}AsO(OH)_2$: C, 30.61; H, 6.84. Found: C, 30.21; H, 6.63.

The magnesium salt was easily prepared by boiling the acid with magnesium mixture. *Isoamylarsonic acid* is a pearly white crystalline substance that melts at 194°; 100 cc. of a saturated aqueous solution at 28° contains 0.820 gram; an equal quantity of a saturated alcoholic solution at 21° contains 2.2 grams. Like the other arsonic acids it is insoluble in ether.

Isoamylarsine Disulphide.—This sulphide was prepared as was the normal propyl disulphide. It is a viscid, light-yellow oil that will not solidify in a freezing-mixture and cannot be distilled without decomposition. The analysis gave 30.62 per cent. of S. Calculated for $C_5H_{11}AsS_2$, 30.48 per cent.

Benzylarsonic Acid.—Of all the arsonic acids, this is the most easily prepared. When quantities of the substances indicated by the equation,

$$2C_6H_5CH_2I + As_2O_3 + 6KOH = 2C_6H_5CH_2AsO(OK)_2 + 2KI + 3H_2O,$$

are dissolved in a mixture of alcohol and water in the manner previously described, freed from the alcohol by distillation, first neutralized and then carefully acidified with hydrochloric acid, a precipitation of *benzylarsonic acid* to the extent of 60 per cent. occurs.

Benzylethyl ether, equal to the loss of benzyl iodide not fixed by the arsenite, may be recovered from the alcohol removed by distillation[1]. Upon washing the free acid with water and recrystallizing once from water or alcohol it is easily obtained pure. The analysis gave: C, 38.65; H, 4.20. Calculated for $C_6H_5CH_2AsO(OH)_2$: C, 38.88; H, 4.16.

Benzylarsonic acid crystallizes in long, beautiful, white, glistening needles. It melts at 167°. It dissolves with difficulty in cold water but is quite easily soluble in hot water; 100 cc. of a saturated aqueous solution at 22.5° contains 0.34 gram; at 27°, 0.39 gram; and at 97° contains 3.50 grams of the acid. Its solubility in alcohol is indicated by the following data: 100 cc.

[1] Am. Ch. J. 33, 142.

of a saturated alcoholic solution at 23° contains 0.87 gram of acid and at 70°, 5.91 grams of the acid. It is stable in the air, has no odor but has a peculiar bitter taste. It has an irritating effect upon the epidermis and the mucous membrane. An aqueous solution of the acid gives with silver nitrate a white precipitate of the silver salt, and with magnesium mixture on boiling, a white precipitate of the magnesium salt.

Benzylarsine Disulphide.—Treated with hydrogen sulphide benzylarsonic acid slowly precipitates the benzylarsine disulphide, $C_6H_5CH_2AsS_2$, which is very similar in properties to the arsine disulphides previously described. It is a heavy, bright-yellow oil that dissolves rapidly in nitric acid, liberating sulphur and oxides of nitrogen. On being heated alone it gives off hydrogen sulphide and forms arsenic trioxide and stilbene. The reaction is, probably:

$$2C_6H_5CH_2AsS_2 = C_6H_5CH{=}CHC_6H_5 + As_2O_3 + H_2S.$$

Decomposition of Benzylarsonic Acid by Heat.—Benzylarsonic acid on being heated yields the following decomposition products: Benzyl alcohol, benzaldehyde, stilbene, water and arsenic trioxide. Probably the most important reaction is:

$$2C_6H_5CH_2AsO(OH)_2 = C_6H_5CH_2OH + C_6H_5CHO + As_2O_3 + 3H_2O,$$

while stilbene is formed in smaller quantities according to the equation:

$$2C_6H_5CH_2AsO(OH)_2 = C_6H_5CH{=}CHC_6H_5 + As_2O_3 + 3H_2O.$$

Upon heating the corresponding arsinic acid, $(C_6H_5CH_2)_2AsOOH$, Michaelis and Paetow[1] found that it decomposed according to the following reaction:

$$2(C_6H_5CH_2)_2AsOOH = As_2 + 2H_2O + 2C_6H_5CHO + (C_6H_5CH_2)_2.$$

When 50 grams of benzylarsonic acid, containing some water of crystallization, were heated in a small flask attached to a condenser, an emulsion having the odor of benzaldehyde passed over. On standing, 15 grams of water separated. The oil was shaken with a concentrated aqueous solution of sodium bisulphite until the odor of benzaldehyde was discharged, and was then extracted with ether. On acidifying and distilling with steam, the aqueous solution was easily proved to contain benzaldehyde. The ether solution, after drying with calcium chloride, was distilled and gave a fraction which boiled largely between 200° and 210° (benzyl alcohol boils at 206°). This fraction was

[1] Ann. **233**, 83.

treated with acetyl chloride and benzoyl chloride and yielded benzyl acetate (106°) and benzyl benzoate (329°) respectively. The quantities of benzyl alcohol and benzaldehyde produced were approximately equal; therefore, the following reaction is established:

$$2C_6H_5CH_2AsO(OH)_2 = C_6H_5CH_2OH + C_6H_5CHO + As_2O_3 + H_2O.$$

A higher fraction boiling between 300° and 310° was obtained, (stilbene boils at 306° and dibenzyl boils at 284°). It was, however, too small in quantity to be purified by fractionation and it could not be crystallized by cooling in a freezing-mixture. A combustion gave:

	Substance.	Calculated for stilbene.	Calculated for dibenzyl.	Calculated for benzyl alcohol.
C	84.65	93.34	92.30	77.07
H	7.95	6.66	7.70	7.64

Evidently the higher fraction was a mixture of benzyl alcohol and stilbene rather than benzyl alcohol and dibenzyl. Further evidence for this conclusion is seen in its easy decolorization of bromine water. Therefore it may safely be held that a secondary decomposition of benzylarsonic acid by means of heat is:

$$2C_6H_5CH_2As(OH)_2 = C_6H_5CH{=}CHC_6H_5 + As_2O_3 + 3H_2O.$$

Decomposition of Benzylarsonic Acid by Acids.—Unlike its homologues and isologues, benzylarsonic acid is easily decomposed by mineral acids. Michaelis and Paetow[1] observed that concentrated hydrochloric acid completely decomposed dibenzylarsonic acid into arsenic trichloride, benzyl chloride and toluene, according to the equation:

$$(C_6H_5CH_2)_2AsOOH + 4HCl = C_6H_5CH_2Cl + C_6H_5CH_3 + AsCl_3 + 2H_2O.$$

With concentrated hydrochloric acid we find that benzylarsonic acid is decomposed into benzyl chloride and arsenious acid (no toluene was detected), therefore the reaction is:

$$2C_6H_5CH_2AsO(OH)_2 + 2HCl = 2C_6H_5CH_2Cl + As_2O_3 + 3H_2O.$$

With sulphuric acid we find that dibenzyl, benzaldehyde, and arsenious acid are the decomposition-products, therefore, the following reaction is probable:

$$4C_6H_5CH_2AsO(OH)_2 = (C_6H_5CH_2)_2 + 2C_6H_5CHO + 2As_2O_3 + 4H_2O.$$

The speed of the above reaction may be determined by titration with a standard iodine solution, free iodine having no effect on

[1] Ann. 233, 84.

arsonic acids. The accompanying table shows the great speed of the decomposition:

Weight of benzyl-arsonic acid.	H_2O. cc.	H_2SO_4. cc.	Time. Minutes.	Temperature.	Decomposition. Per cent.
1.500	25	10	30	100°	100
1.500	25	10	15	100	100
1.318	25	5	5	100	99
1.318	25	5	5	100	99.4
1.172	25	1	10	100	92

The decomposition with sulphuric was much more rapid than with hydrochloric acid. When phenyl- and ethylarsonic acids were treated in the same manner only traces of arsenious acid were detected.

Decomposition of the Salts of Fatty Arsonic Acids by Heat.—It was found by Dehn[1] that heat decomposed magnesium ethylarsonate into magnesium oxide, metallic arsenic, water and a hydrocarbon gas.

A closer study of this decomposition was made by us and it was found that the hydrocarbon gas given off is a mixture of methane and ethylene. The unsaturated gas was separated from the methane by treatment with bromine water, and the ratio of their volumes was found in one case to be 42.5 per cent. of the former to 57.5 per cent. of the latter. A combustion of the residual gas gave the following data:

43.5 cc. of gas (corrected and equal to 0.0317 gram) gave 0.0863 gram of CO_2 and 0.0714 gram of H_2O.

	Calculated for CH_4.	Found.
Carbon	75.00	75.10
Hydrogen	25.00	24.04

An analysis of the saturated gas by the explosion method gave the following results:

	Vol. gas saturated.	Vol. CO_2 theory.	Vol. CO_2 found.	Vol. H_2O theory.	Vol. H_2O found.
I.	10.2	10.2	10.4	20.4	20.4
II.	12.0	12.0	11.8	24.0	24.2

Evidently, the saturated gas is methane.

An analysis of the mixture of saturated (57.5 per cent.) and unsaturated (42.5 per cent.) gases was made by the explosion method and gave the following data:

[1] Am. Ch. J. 33, 133.

	Volume gas saturated and unsaturated.	Volume CO_2 calculated.	Volume CO_2 found.	Volume H_2O calculated.	Volume H_2O found.
1.	8.4	12.0	11.8	16.8	16.6
2.	9.0	12.0	12.8	18.0	18.2

This indicates that the unsaturated gas is ethylene. An equation proposed to represent the decomposition of magnesium ethylarsonate is as follows:

$$(C_2H_5AsO_3Mg)_2H_2O = 2CH_4 + C_2H_4 + Mg_2As_2O_7.$$

This, however, cannot represent the entire reaction, for water is formed as well as a larger quantity of ethylene than is indicated by the equation. As magnesium ethylarsonate is dehydrated and partially decomposed at 145–170°,[1] the following secondary reaction may occur:

$$2C_2H_5AsO_3Mg = C_2H_4 + H_2O + Mg_2As_2O_5.$$

Furthermore as carbon dioxide (10–18 per cent. of the evolved gases) and metallic arsenic are found among the end-products, other reactions are probably necessary to represent the complete decomposition.

Decomposition of Magnesium n-Propylarsonate by Heat.—When magnesium *n*-propylarsonate was heated in an apparatus filled with carbon dioxide, it yielded a gaseous product which, when freed from carbon dioxide, was soluble in bromine water to the extent of 40 per cent.; therefore this gaseous product consisted of 40 per cent. of an unsaturated hydrocarbon and 60 per cent. of a residual gas whose analysis indicated a mixture of hydrogen with methane. In the analysis given below, the gas in experiment (*a*) was obtained from the total evolved gas, while in experiment (*b*) the gas was obtained from that last evolved during the heating of the arsonate.

(*a*)	Volume gas.	Volume CO_2 found.	Volume H_2O found.	Volume H_2O calc. for H_2.	Volume H_2O calc. for CH_4.	Volume CO_2 calc. for CH_4.
1.	15.0	8.6	25.4	15.0	30.0	15.0
2.	11.5	6.2	18.6	11.5	23.0	11.5
3.	12.0	6.9	19.8	12.0	24.0	12.0

This experiment shows that the saturated gas consists of nearly equal parts of hydrogen and methane.

(*b*)	Volume gas.	Volume CO_2 found.	Volume H_2O found.	Volume H_2O calc. for H_2.	Volume H_2O calc. for CH_4.	Volume CO_2 calc. for CH_4.
1.	10.8	7.8	14.1	10.8	21.6	10.8
2.	10.2	7.0	13.2	10.2	20.4	10.2
3.	10.7	7.3	13.7	10.7	21.4	10.7

[1] Am. Ch. J. 33, 133.

This experiment shows about 70 per cent. of methane and 30 per cent. of hydrogen.

When 40 grams of magnesium *n*-propylarsonate were heated so that the gaseous products were passed through bromine water, a quantity of halogen-olefine addition-product was obtained. Distillation of the oil yielded fractions that boiled near the boiling-points of ethylene bromide (129.5°) and propylene bromide (141°).

Analysis of the first fraction by the Carius method gave 85.35 per cent. Br; calculated for $C_2H_4Br_2$, 85.11 per cent.

The second fraction gave 78.42 per cent. Br; calculated for $C_2H_5BrCH_2Br$, 79.71 per cent.

The above experiments prove the presence of hydrogen, methane, ethylene, and propylene. However, at present, the evidence on the decomposition of magnesium *n*-propylarsonate is too slight to venture writing the equations involved.

Meyer's Reaction.—The above-described arsonic acids were prepared by Meyer's reaction, that is, by application of the following general reaction:

$$RX + K_3AsO_3 = K_2RAsO_3 + KX.$$

Evidence for their formation was obtained in preliminary experiments[1] by determination of the per cent. of transformation of arsenite. Other preliminary studies along this line are given below.

Haloid derivative.	Time. Hours.	Temperature.	Yield. Per cent.
Isobutyl iodide.....	2	25°	5
" "	4	25	9
" "	32	25	10
" "	100	25	10
" "	0.5	80	12
" "	3	80	12
Chloroform	1	25	1
"	4	25	1
"	45	25	4
"	98	25	4.8
Bromoform	1	25	5
"	42	25	15
"	53	25	23
"	96	25	30
"	216	25	30

[1] Am. Ch. J. 33, 138.

Haloid derivative	Time. Hours.	Temperature.	Yield. Per cent.
Iodoform	26	23	35.4
"	40	23	50
"	51	23	52.9
"	94	23	79
"	114	23	81.5
"	210	23	92.2
"	0.5	80	50
"	1	80	51
"	2.5	80	54
"	15	80	86
p-Chlortoluene	1	25	0
"	42	25	3
"	96	25	3
Allyl iodide	0.2	25	39
" "	0.5	25	45
" "	1	25	46
" "	26	25	51

These determinations were made by titrating the unchanged potassium arsenite with standard solutions of iodine, and thus determining by difference the quantity which had been transformed into the arsonic acid. The allyl iodide appeared to act abnormally, first a brown precipitate being formed, and then a yellow oil.

It is evident from these experiments that other arsonic acids besides those hitherto described may easily be prepared.

Properties of the Arsonic and Arsinic Acids.—All of these acids are beautiful white crystalline substances which are usually quite easily soluble in water and alcohol and are almost insoluble in ether.

Solubilities and melting-points as determined by us are given in the accompanying table:

Acid.	Solvent.	Temperature.	Soluble in 100 parts.	Melting-point.
Ethylarsonic.	Water.	27°	70.00	99.5°
" "	"	40	112.00	.....
" "	Alcohol.[1]	25	39.40	.....
Propylarsonic.	Water.	26	43.00	125.0
Isoamylarsonic.	"	28	0.82	194.0
" "	Alcohol.	21	2.20	.....
Benzylarsonic.	"	23	0.87	167.0
" "	"	70	5.91	.....
" "	Water.	22.5	0.34	.....

[1] The alcohol used in these experiments was of 95 per cent. concentration.

Acid.	Solvent.	Temperature.	Soluble in 100 parts.	Melting-point.
Benzylarsonic.	Water.	27	0.39	.....
" "	"	97	3.50	.....
Phenylarsonic.	"	28	3.25	158.0
" "	"	41	4.82	.....
" "	"	52	8.52	.....
" "	"	84	24.00	.....
" "	Alcohol.	26	15.51	.....
" "	"	68	55.40	.....
Methylarsinic.	Water.	22	82.90	.....
Phenylarsinic.	"	27	0.28	164.0
" "	Alcohol.	22	11.80	.....
" "	"	55	57.70	.....

URBANA, ILL., December 27, 1905.

[CONTRIBUTION FROM THE MISCELLANEOUS LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

COPPER SALTS IN IRRIGATING WATERS.[1]

BY W. W. SKINNER.

Received January 11, 1906.

THE Miscellaneous Laboratory of the Bureau of Chemistry has for several years past been engaged in a study of the effect of certain waste products from manufacturing operations in regard to their injurious effect upon vegetation and agricultural crops. "The Injury to Vegetation by Smelter Fumes," by J. K. Haywood is the first of a series of bulletins upon this subject. Supplementing this work and as a logical sequence thereto, a study of other waste products from smelters, concentrating plants, and mining operations naturally follows. The data submitted in this paper relate only to copper operations, and the injurious effect upon vegetation from copper salts which, as a waste product from the mining and reduction of copper ores, are frequently carried into and contaminate water supplies which later are used for irrigation purposes.

Toxicity of Copper Salts.—The extremely toxic character of copper salts to plant life is a subject that has received considerable attention both in this country and by foreign investigators. Johnson[2] remarked years ago the injurious effect of salts of copper,

[1] The second of a series of studies by the Miscellaneous Laboratory on trade wastes in their relation to agriculture. Read at the New Orleans Meeting of the American Chemical Society.

[2] "How Crops Grow," Johnson.

lead and zinc upon plant life. Nageli[1] has found that copper in merest traces is toxic to growing plants, while Low[2] has shown that even the very slight amount of copper which goes into solution during the process of obtaining distilled water from a copper still is injurious to plants when the water is used in culture experiments.

Harter[3] states as a result of his observations that copper is one of the most toxic substances known.

The degree of toxicity of the several salts experimented with varies with the character of the plants, some salts being very much more toxic to some plants than to others, and while all authorities agree that copper salts are extremely toxic, they do not all agree upon the exact coefficient of toxicity. This lack of concordance in results is due no doubt to the different conditions of experiment and to the different plants used. The variation of different plants in respect to their resistance to salts has been clearly demonstrated in the work of Harter above referred to, in which he shows that with several salts, the one that is most toxic for any one plant, say for instance corn, is not necessarily the most toxic for other plants such as wheat or peas.

As to the amount of copper which is toxic, Coupin[4] states that 1 part of copper in 700,000,000 parts of water is sufficient to retard the root growth of wheat seedlings, and that a mere trace of this substance is in many cases sufficient to retard growth. Heald[5] in his experiments demonstrated that seedlings of *Pisum sativum* were killed when the solution contained 1 part of copper in 404,423 parts of water, and that *Zea Mais* seedlings were killed in a solution, the concentration of which was 1 part of copper in 808,846 parts of water.

In all of the above experiments the toxicity was determined in water cultures. The considerations leading to the adoption of water culture methods are purely those of expediency. The results are more definite and the control of disturbing factors are, under such conditions, more easily managed than would be possible with soil cultures. That the toxic coefficients so deter-

[1] Denkschr. schweizerischen Naturf. Ges. 33, 1.
[2] Land. Jahrb. 20, 235.
[3] U. S. Dept. Agr., Bur. Plant Ind., Bull. 79, p. 40.
[4] Rev. gén. botanique, 10, 180.
[5] Bot. Gaz. 22, 142.

mined do not hold true in their entirety for soil solutions is not to be denied, for it is a well known fact that the other salts found in the soil solution may either by a stimulating action upon plants, or by a partial neutralization of the toxicity of the salt materially reduce the effect of the latter. The mutual effect of some of the so-called alkali salts upon one another has been very carefully worked out by Cameron and Kearney,[1] in some instances with very surprising results. For instance, they found that of the several alkali salts magnesium sulphate was the most toxic to plants, when cultivated in pure solutions of this salt. It was much more toxic than sodium carbonate or sodium chloride. When, however, lime salts were present they found that the relative toxicity of these salts was exactly reversed, magnesium sulphate being the least harmful of the alkali salts. This latter conclusion entirely agrees with actual field observations.

Water cultures, however, do determine the maximum coefficient of toxicity for any particular salt for the particular plant experimented upon, and as it is the maximum factor which must be considered when arriving at any practical conclusion, the knowledge so gained is of the highest importance.

Copper Salts as a Waste Product.—In no phase of mining has greater progress been made in recent years than in the working of low-grade copper ores. Deposits of large extent that a few years ago were considered of entirely too low grade to be worked with profit, are now experiencing an unusual development. This is in large part due to the perfecting of mining machinery for working such low-grade ores. Concentrating machinery of both the wet and dry types are in use, but up to the present time only the wet method of concentrating has been entirely satisfactory. For the successful application of this method large quantities of water are necessary. The laws governing water rights in most western states allow the mining and milling companies to use the water of the streams for their operations, but as the water belongs to the land, title to it can only be obtained through title to the land. Hence the mining and milling companies are required to return the water after use to the main waterway, without materially interfering with its use for irrigation purposes. But in the operation of copper concentrating plants this is a difficult matter to accomplish. In such an operation as concentrating

[1] U. S. Dept. Agr., Rept. 71.

it is generally impracticable to remove all the copper. It may happen therefore that anywhere from 0.25 per cent., or less, to 1.5 per cent. of copper may remain in the tailings which are carried on the dump, or directly into the stream and thence upon the irrigated land. The extremely fine condition of the tailings and the moisture conditions in the dump are such as to render oxidation of the copper therein quite rapid, as is also the case with the fine tailings which are carried upon the land by the irrigating water. It is not unusual therefore, as might be expected, to find the leachings from a dump of sulphide ores to contain large amounts of copper in the form of sulphate. This sulphate, together with the fine tailings introduced directly into the water which is to be used later for irrigating, is a cause for serious consideration to the land owner and irrigator when it is realized, as has been pointed out above, how extremely toxic copper salts are.

The Chemical Problem.—A priori, one might assume that with the large amounts of carbonates and bicarbonates of the alkaline earths and sometimes the alkalies found in soils of the arid and semiarid region, the injurious effect of the application of copper salts would not be very great until at least a large portion, if indeed not all, of the carbonates had reacted with these salts to form insoluble compounds of copper. And that it would be only after this reaction was satisfied that the copper would remain in a condition to affect plant life. Actual field observations prove, however, that this is not the case, and that injury does occur even when the soil solutions are known to contain relatively large amounts of bicarbonates of calcium, magnesium, etc. That the injury is due to the effect of copper has further been confirmed by the author and others who have found water-soluble copper in soils under conditions noted above, and an absence of sufficient amounts of alkali salts to produce upon vegetation the toxic effect noted.

There are therefore two distinct features of the problem,—the solubility of copper salts in solutions of normal carbonates and the solubility of copper salts in solutions of bicarbonates. If a solution of a carbonate, for instance sodium carbonate, is added to a solution of a copper salt "normal carbonate of copper does not occur but only the basic salts."[1] The first result is

[1] Ostwald: "Principles of Chemistry, Inorganic," p. 636.

green basic carbonate of copper having the composition $CuCO_3.Cu(OH)_2$, which corresponds to the mineral malachite. If more of the sodium carbonate is added, the green precipitate is dissolved, forming a deep blue solution. The solubility of the copper salts in solutions of the normal carbonates, while of considerable scientific interest, is not of great importance in our problem, for it is the exception that normal carbonates are found in soil solutions or irrigating waters, but generally the bicarbonates. However, the reaction with the bicarbonates is entirely analogous to that with the normal carbonates. It is frequently true that both the soil solutions and irrigating waters contain large amounts of bicarbonates, usually of calcium and magnesium and sometimes sodium. In regard to the soil solution it is probable that upon the addition of an irrigating water containing carbon dioxide to a soil containing calcium in the form of carbonate, considerable quantities of the carbonate go into solution as $Ca(HCO_3)_2$. The question therefore of how much copper this bicarbonate will hold in solution is vital. To determine this, several grams of pure calcium carbonate were placed in two liters of water and a current of carbon dioxide passed through the solution for twelve hours. This solution was found to contain at the temperature at which the experiment was conducted (23.5° C.), the equivalent of 1.1075 grams $Ca(HCO_3)_2$ per liter. To one liter of this solution a dilute solution of copper sulphate was gradually added until precipitation just began. The solution was allowed to stand until perfectly clear (about forty-eight hours). All the precipitated basic copper carbonate having settled, one liter of the clear solution was then removed, concentrated, and the copper determined electrolytically. The yield of copper was found to be 0.2071 gram per liter.

The reaction between copper salts and the bicarbonates of the alkalies is believed to be, from an irrigation standpoint, of secondary importance as compared to the reaction with calcium and magnesium bicarbonates; however it is not unusual to find the alkali carbonates and bicarbonates existing in both irrigating waters and soil solutions. While both the soil and the irrigating water may contain the normal carbonate, yet in the practice of irrigation it is entirely probable that these salts very rapidly revert, at least in great part, to the bicarbonate. Especially does this seem plausible when it is remembered that the river

waters of the west from which irrigation supplies are taken as a rule carry large amounts of dissolved carbon dioxide.

To determine the solubility of copper salts in the alkali bicarbonates the following experiment was conducted. To about 2 liters of water was added pure sodium bicarbonate until several grams remained in the solid phase. Through the saturated solution a current of pure carbon dioxide was passed for twelve hours, the solution allowed to settle until clear, when it was tested and found to contain no normal carbonate. A portion was drawn off and a dilute solution of copper sulphate added until a permanent precipitate just occurred. The solution was then allowed to settle until clear, requiring about forty-eight hours, and the copper determined in the clear solution as before by the electrolytic deposition from a nitric acid solution. The copper held in solution was found to be 953 parts per million. It may be objected that in actual irrigation practice the soil solution never reaches anything like the concentration of the solution with respect to sodium bicarbonate given above, and it is undoubtedly true that if a soil solution should, at its maximum dilution, contain anything like this amount of the bicarbonate, plant life would be inhibited. When, however, water is added to a soil the soluble salts very soon go into solution, and as capillarity brings the water to the surface and evaporation proceeds, the concentration gradually increases until, if the loss of moisture continues to completeness, it is readily seen that the saturation point of every salt held in solution is reached. It is apparent therefore that the solution of any toxic salt in a saturated solution is of vital interest and must be considered as well as the solubility in more dilute solutions.

To determine, however, the amounts of copper held in solution by a dilute solution of sodium bicarbonate, which more nearly approached conditions as sometimes met in the soil, the following experiments were made. A solution was made of sodium bicarbonate of a strength corresponding to a soil solution which would result from adding one-third of an acre foot of irrigating water to one acre of soil containing 0.05 per cent. of sodium carbonate, assuming that the latter would be converted to the bicarbonate, and also another solution of half this strength or representing a soil containing 0.025 per cent. of sodium carbonate.

These amounts of sodium bicarbonate were taken because they are respectively one-half and one-quarter of that quantity of this salt, which under ordinary irrigation practice has been demonstrated to be about its toxic limit for most farm crops. The results are tabulated with those preceding and are as follows:

Solution $NaHCO_3$.	Parts per million of copper held in solution.
A. Saturated	953.00
B. Solution equivalent to soil containing 0.05 per cent. Na_2CO_3	1.70
C. Solution equivalent to soil containing 0.025 per cent. Na_2CO_3	0.40
Solution containing $Ca(HCO_3)_2$ 1.1075 grams per liter	207.10

An inspection of this table reveals the fact that even with a dilute solution of sodium bicarbonate, where the amount, if present in a soil solution, would not condemn the land for most agricultural crops, there was held in solution a quantity of copper entirely sufficient to be toxic to plants and in some cases sufficient to inhibit plant growth. The results, however, with calcium bicarbonate are believed to be of more importance than those with sodium bicarbonate, for the former may exist in a soil solution in very much greater quantities without any effect upon plants, than is the case with the bicarbonates of the alkalies. And, furthermore, as most arid soils contain large amounts of calcium in the form of carbonate, as before stated it is entirely reasonable to assume that where the irrigating water contains much dissolved carbon dioxide the soil solution soon becomes relatively highly charged with this salt. The fact that a solution of this salt of the strength before given should hold in solution 207.1 parts of copper per million, is believed therefore to be of considerable significance and offers an explanation of the phenomenon observed in actual field practice as to the destruction of vegetation when irrigated with a water containing soluble copper salts, even though the application be made to soils containing calcium, magnesium and other carbonates.

SUMMARY.

(1) It has been demonstrated by Coupin, Nageli, Löw, Harter and others that for most plants, copper is one of the most toxic substances known.

(2) For wheat seedlings 1 part of copper to 700,000,000 of

water has been found to retard growth, and 1 part in approximately 800,000 was fatal to the growth of corn.

(3) One part of copper per million of water should condemn the water for irrigation purposes.

(4) Copper salts are not rendered entirely insoluble when brought into contact with solutions containing carbonates and bicarbonates, and there may be held in solution under such conditions sufficient copper to be toxic to plants.

(5) That the solubility of copper in solutions of bicarbonates probably explains the observed injury produced by irrigating waters carrying copper, even when applied to soils containing large amounts of carbonates and bicarbonates.

THE DETERMINATION OF SMALL QUANTITIES OF COPPER IN WATER.

(Published by permission of the Director of the U. S. Geological Survey.)

BY EARLE B. PHELPS.

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DURING the past few years the question of the addition of small quantities of copper salts to water supplies as a preventative of algal growths and as an emergency disinfectant against typhoid fever germs, has received much discussion and led to many important investigations in this country as well as abroad. One result of all this work has been to indicate the need of some simple yet accurate method for the determination of the small amounts of copper with which the investigator has to deal. The method recommended by the Committee on Standard Methods of Water Analysis of the Laboratory Section of the American Public Health Association,[1] is essentially that of Clark and Forbes.[2] It involves the concentration of a sufficient amount of the water to yield a weighable amount of copper, the precipitation of the copper as well as of certain other metals which may be present, as sulphides, and the separation from the mixed sulphides of the lead and iron by the usual methods. The copper is then deposited electrolytically and weighed. Quantities of copper as small as 2 or 3 mg. are thus determined by Clark and Forbes with a mean probable error of about 5 per cent., while the de-

[1] "Report of the Committee on Standard Methods of Water Analysis," Jour. Inf. Dis. 1905, Sup. No. 1, p. 1.

[2] Mass. State Board of Health, 32d Ann. Rep. for 1900, p. 487.

termination of 1 mg. obviously cannot be made with a probable error of less than 10 per cent. The disadvantages of the process are, first, the necessity for boiling down a large volume of water in order to get sufficient copper to weigh with accuracy, and, second, the length of time required and the liability of error introduced by the precipitations and separations involved.

Colorimetric methods, while generally much more sensitive than the gravimetric, are greatly influenced by the presence of other substances, especially other metals and organic coloring-matter.

The writer has had occasion to make a number of such copper determinations and was moreover limited by the experimental conditions to quantities of one liter for each determination. Since the water contained at times only a few tenths of a milligram of copper per liter, the standard method of procedure was obviously out of the question. As a result of a study of various possible methods for the determination, a procedure was devised which seemed to combine to a satisfactory degree the requisite sensitiveness, accuracy and simplicity. The method consists in the evaporation of a given volume of the water to about 100 cc. the electrolytic separation of the copper from the acidulated solution, the solution of the deposited copper in dilute acid, and its neutralization and colorimetric determination as sulphide, by comparison with standard tubes of known copper content. By this procedure it is easily possible to determine 0.1 mg. of copper, or if this amount were derived from a liter of water, 0.1 part per million. The accuracy is fully as great as with the gravimetric method using ten times as much of the same water.

The detailed procedure is as follows:

Apparatus.—Platinum dishes of about 100 cc. capacity to serve as anodes. Connection with the circuit is most conveniently made by placing the dish in a little mercury, contained in a shallow metal dish. To the latter is soldered a wire leading to the positive binding post.

A stout platinum wire, about 50 cm. long, 40 cm. of which is coiled into a flat spiral and whose end is fastened directly to the negative binding post. The spiral constitutes the cathode.

A convenient source of electrical current. The character of the current is not so important in this case as in gravimetric processes, since only small amounts of copper are dealt with and

SUMMARY OF COPPER DETERMINATIONS.

No.	Water.	Parts per million. Total solids.	Loss on ignition.	Characteristics of the water.	Substances added.	Mg. of copper. Taken.	Found.
1	Boston tap water....	40	15	Soft, colored, surface.	None.	0.54	0.52
2	Boston tap water....				None.	0.27	0.27
3	Boston tap water....				None.	0.27	0.24
4	Boston tap water....				None.	0.14	0.12
5	Boston tap water....				None.	0.14	0.12
6	Boston tap water....				Fe as $FeCl_3$, 5 mg.; Pb as acetate, 40 mg.	0.54	0.54
7	Boston tap water....				Ag as $AgNO_3$, 0.5 mg.; Sn as $SnCl_2$, 1.0 mg.	0.54	0.57
8	Chattahoochee, Ga..	300	50	Soft; solids are red iron clay.	None.	0.54	0.57
9	Pecos, N. Mex.....	2000	100	Hardness of 840 parts; turbid.	None.	0.54	0.54
10	Milk, Mont.....	750	.....	Hardness of 620 parts; clear.	None.	0.54	0.55
11	Colorado, Tex.....	300	.....	Hardness of 128 parts; turbidity of 110.	None.	0.54	0.52
12	Boston sewage..	4000	810	Chlorine abnormal, about 1500.	None.	0.54	0.50
13	Hay infusion.....	.....	.....	Color about 300.	None.	0.54	0.55
14	Straw board waste..	7000	4000	High in CaO and organic acids.	None.	0.54	0.51

the deposit need not be washed or dried. In the present experiments the current was supplied by two "gravity cells" in series, yielding a current through the solution of about 0.02 ampere. The current density at the cathode was about N. D_{100}=0.3 ampere.

Nessler jars of the short type holding 100 cc.

Reagents.—Standard copper solution. About 0.8 gram of clean copper sulphate crystals are dissolved in water and, after the addition of 1 cc. concentrated sulphuric acid, the volume is made up to one liter. In 100 cc. of this solution the copper is determined in the usual way by electrolytic deposition and weighing and the solution is diluted so that 1 cc. contains 0.2 milligram copper. This solution is permanent.

Potassium sulphide reagent. An alkaline solution of potassium sulphide made by mixing equal volumes of 10 per cent. potassium hydroxide solution, and a saturated solution of hydrogen sulphide in water.

Nitric acid one to three and sulphuric acid one to one, both tested for copper.

The Determination.—Of waters carrying from 0.1 to 1.0 part copper one litre is taken. For other concentrations take proportionate amounts. Evaporate to about 75 cc. and wash into the platinum dish. Add 2 cc. of the dilute H_2SO_4 for clear and soft waters. For alkaline waters an additional amount is used to offset the alkalinity. For waters carrying much organic matter or clay, 5 cc. of acid are added to assure the formation of a soluble copper salt. The dish is then placed in position, the cathode suspended in the solution so that it is parallel to and about half an inch from the bottom, and the circuit is closed. Electrolyze for about four hours with occasional stirring, or over night, if convenient. Lift out the cathode without previously having opened the circuit, and immerse the spiral in a small amount of the dilute nitric acid, previously heated to boiling. Wash off the wire and evaporate the nitric acid solution to dryness on the water-bath. If silver is suspected to be present, add a few drops of hydrochloric acid before evaporation. Take up in water and wash into the Nessler jar. Make up to the mark and add 10 cc. of the sulphide reagent. The color of the copper sulphide develops at once and is fairly permanent, lasting for several hours, at least. A similar tube is prepared

by adding 10 cc. of the reagent to a tube of distilled water and then adding standard copper solution in 0.2 cc. portions until the colors of the two tubes match. If one litre of water were originally taken, each cubic centimeter of standard solution used represents 0.2 part per million of copper.

The method has been carefully tested as to the completeness of the separation and as to the influence of other substances in the water. Particular care has been taken to separate small amounts of copper from large amounts of organic matter (sewage and industrial wastes), coloring-matter in surface waters, and from salts of iron, lead, silver and tin. As will be seen from the appended table of results the separation is in all cases satisfactory. Silver and tin appear to be, according to the authorities, the only metals which will separate out under the conditions used. Neither will be commonly met with. The silver may be converted into the chloride as indicated and does not interfere with the determination. The tin is only partially dissolved by the nitric acid and during the evaporation is converted into metastannic acid. In the alkaline solution used in the test the tin in this form does not interfere in the least.

In the accompanying table are given the results obtained in testing this method. In all cases except those in which Boston sewage and straw-board liquor (the waste liquor of a straw-board mill) were used, one litre of water was taken and the necessary solutions added to it. In the two cases mentioned only 100 cc. were taken.

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SOME INVESTIGATIONS ON SALTS OF CASEIN.[1]

BY J. H. LONG.

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THE question of the identity of caseins from different kinds of milk is an old problem for which the complete solution appears to be still some distance in the future. Even superficial observation suggests that in the milks from different animal species the peculiar coagulating substance is characteristic. From cow's milk, for example, by acid or rennet coagulation what is loosely termed "casein" is thrown down in large flakes. From

[1] Read at the New Orleans Meeting of the American Chemical Society.

human milk, on the other hand, the curd formed by acid or rennet is extremely fine, so fine indeed, that it may even be overlooked. These physical differences may be due to actual differences in constitution, or they may be due to the presence of other protein substances thrown down at the same time. In respect to this behavior with acid or rennet cow's milk and human milk seem to represent the extremes; the "caseins" of the other milks fall in between them, apparently.

This question of the nature of casein, and the relation of the substance as it exists in mother's milk to that from cow's milk is an important one from the practical standpoint, as the difficulties of providing a proper artificial milk diet for infants is assumed to depend largely on the peculiarities of the casein from cow's milk which is naturally taken as the basis of the various substitute foods prepared. Some years ago I undertook a series of experiments to determine by physical methods certain constants which might be considered as characteristic for each casein. For the time these experiments were interrupted and only recently resumed.

At the outset there is presented the problem of the preparation of pure casein, and we are confronted at once with the question of the definition of "casein" and by what general method the product should be separated from milk. In the Hammarsten method, as applied to cow's milk, the latter is largely diluted and precipitated by a little acetic acid. The supernatant liquid is poured off and the precipitate taken up with very weak alkali, preferably ammonia or sodium carbonate. This solution is largely diluted and precipitated again with weak acetic acid, these operations being repeated five or six times. The product is finally filtered, washed with water, then with alcohol and lastly with ether. The pure casein is air-dried and finally *in vacuo* over sulphuric acid. It holds then about 2 per cent. of moisture, which may be expelled at 105°.

But this whole series of operations must be carried out with great care to yield a suitable product. Not only must the acid and alkali solutions used be very weak but the operations must be quickly performed. Following each treatment a large volume of distilled water must be used, but in a prolonged contact with this water there is great danger of producing a modified or "denatured" casein which is no longer readily soluble in weak

alkali. As a basis for the preparation it is well to use thoroughly skimmed milk. In my experiments with cow's milk I used milk from which all but about 0.1 per cent. of the fat had been separated by the centrifugal process. The final alcohol and ether washings, like the water washings, should be quickly performed and there is an advantage therefore in using such milk.

This general process may be applied to different kinds of milk with different degrees of success. I have succeeded in obtaining excellent products from cow's milk and goat's milk by it, but as applied to human milk the results have been less satisfactory. Besides this, it is not certain that the products obtained are quite the same as would be secured by beginning the separation with rennet and following this up with solution and reprecipitation; but for purposes of comparison I have thought it best to prepare all the products by the same process, which should be as simple as possible.

With caseins obtained as briefly outlined a number of general tests may be made, and from these a series of constants determined which will serve for comparison of different products. Among the several determinations the following may be carried out:

(*a*) The equivalent weight by titration with N/10 alkali, using phenolphthalein.

(*b*) The electrical conductivity of the salt solutions so obtained, and of salt solutions made with half this amount of alkali.

(*c*) The optical rotation of the salt solutions.

(*d*) The behavior of the casein on digestion with pepsin and hydrochloric acid, and the changes in the conductivity of the digesting mixture.

In what follows the results of some experiments in these directions will be given.

A. CASEIN FROM COW'S MILK.

Equivalent Weight.—There are in the literature a number of determinations on this point.[1] As the pure casein expels carbon dioxide Soeldner determined the amount of gas driven off from calcium carbonate. An equivalent of 1120 was found. The same author obtained an equivalent weight of 1205 by titration with lime-water or sodium hydroxide, using phenolphthalein.

[1] See valuable paper by Raudnitz, in Ergebnisse der Physiologie, 2, 221, for many references.

Courant found by the last method a weight of 1053. Laqueur and Sackur,[1] as a mean from the titration of caseins from several sources, found an equivalent weight of 1135. Other results reported differ rather widely, suggesting, probably, lack of care in the preparation of the casein used.

As a further contribution to this topic I have made a large number of titrations of three caseins obtained at different times by the Hammarsten method. These products were so pure that they furnished a very nearly clear solution in weak alkali, and could be polarized without difficulty, as referred to below. The amount of ash in these preparations was about 0.6 per cent. For each titration 5 grams (anhydrous) were weighed into a stoppered flask, about 25 cc. of carbon dioxide-free water and a little phenolphthalein were added and then N/10 alkali, until after thorough shaking a faint color remained. This required 44.5 cc. of the sodium or potassium hydroxide; with 45 cc. the color was always distinct. Assuming 44.5 cc. as sufficient for the reaction this gives an equivalent weight of 1124. Care was always taken to exclude the carbonic acid as well as possible during the titrations. This number lies between the values given by Soeldner and by Laqueur and Sackur, but the caseins were not in either case calculated as ash-free.

By using other indicators different results are, of course, secured. The solution neutral to phenolphthalein is rather strongly alkaline to litmus. In fact, with litmus almost exactly one-half as much alkali is required for the reaction as with phenolphthalein, but the color change is not very sharp. It is possible, however, to just dissolve the casein in exactly half the alkali required for the phenolphthalein neutralization, and in this way I prepared a number of so-called acid salts.

Courant[2] has attempted to distinguish three classes of salts which roughly might correspond to the behavior with three classes of indicators, but the practical isolation of the first class does not seem to be possible. Theoretically, salts of this class would be obtained by titrating to neutrality with lacmoid (or methyl orange), salts of the second class by titrating with litmus, while the salts of the third class are those secured by titrating to neutrality with phenolphthalein, and are the "neutral" salts

[1] Laqueur and Sackur: Beiträge zur chem. Phys. Path. 3, 193.

[2] Courant: Pflüger's Archiv, 50, 109.

as above referred to. It does not follow, of course, that the salts thus obtained are really neutral. We may have here a behavior somewhat like that of the weak phosphoric acid, which in presence of phenolphthalein shows an alkaline reaction when two of the hydrogen atoms are replaced by sodium or potassium. Laqueur[1] rejects the idea of Courant that there may be the three classes of salts, while Fuld[2] quotes it with approval. But in any event it does not help us practically in reaching the molecular weight from the equivalent number.

Electrical Conductivity.—This important physical constant was found for a number of salts, acid and neutral. In making the so-called neutral salts (phenolphthalein) for 5 grams of (anhydrous) casein I used always 45 cc. of N/10 sodium, potassium or ammonium hydroxide and the equivalent amount of lithium carbonate. This insured good solutions which were ready for the test. The conductivities were measured all in the same small Arrhenius cell, having a capacity of 0.3. The usual Kohlrausch method was employed with the large apparatus[3] and calibrated bridge wire. A considerable degree of accuracy is possible in the measurements, and the readings with the telephone may be made with nearly as great certainty as with ordinary salt solutions. This does not seem to agree with the statement of Laqueur.[4] I am unable to account for the difficulty he describes in making duplicate readings. For all the tests a temperature as nearly as possible constant at 20° was maintained. Occasional slight variations were corrected by a factor found as below described.

Conductivity Tables.—In the tables given below the first column contains the concentration of the casein in grams per 100 cc.; the second column the equivalent concentration of alkali; the third column gives the conductivity values κ; in the fourth column are found the values for the equivalent conductivity, $\Lambda = \frac{\kappa}{\eta}$, based on the alkali present. The weaker solutions were in all cases made by dilution of the stronger with water of a high degree of purity obtained by careful distillation and aspiration

[1] Laqueur: Beiträge zur chem. Phys. Path. 7, 274.
[2] Fuld: Ergebnisse der Physiologie, 1, 488.
[3] Kohlrausch und Holborn: Leitvermögen der Elektrolyte, p. 42.
[4] Laqueur: Loc. cit.

of carbon dioxide-free air through the cooled distillate. The water was stored in a flask of hard glass, and protected from the air when drawn off.

NEUTRAL SODIUM SALT, 5 GRAMS OF CASEIN + 45 CC. N/10 NaOH TO 100 CC.

Conc. casein.	$10^6\eta$.	κ_{20}.	$\Lambda = \frac{\kappa}{\eta}$.
5.	45.	0.001787	39.7
2.5	22.5	0.001006	44.8
1.25	11.25	0.000561	49.9
0.625	5.625	0.000310	55.2
0.3125	2.812	0.000172	61.2
0.1562	1.406	0.000093	65.9

ACID SODIUM SALT, 5 GRAMS OF CASEIN + 22.5 CC. N/10 NaOH TO 100 CC.

Conc. casein.	$10^6\eta$.	κ_{20}.	$\Lambda = \frac{\kappa}{\eta}$.
5.	22.5	0.001012	44.9
2.5	11.25	0.000563	50.0
1.25	5.625	0.000308	54.7
0.625	2.812	0.000168	59.8
0.3125	1.406	0.000093	66.1
0.1562	0.703	0.000050	71.1

BASIC SODIUM SALT,[1] 5 GRAMS CASEIN + 67.5 CC. N/10 NaOH TO 100 CC.

Conc. casein.	$10^6\eta$.	κ_{20}.	$\Lambda = \frac{\kappa}{\eta}$.
5.	67.5	0.002694	39.9
2.5	33.75	0.001584	46.8
1.25	16.875	0.000870	51.5
0.625	8.437	0.000480	56.8
0.3125	4.219	0.000264	62.5
0.1562	2.110	0.000144	68.2

BASIC SODIUM SALT,[1] 5 GRAMS CASEIN + 90 CC. N/10 NaOH TO 100 CC.

Conc. casein.	$10^6\eta$.	κ_{20}.	$\Lambda = \frac{\kappa}{\eta}$.
5.	90.	0.003821	42.4
2.5	45.	0.002170	48.2
1.25	22.5	0.001234	54.8
0.625	11.25	0.000700	62.2
0.3125	5.625	0.000380	67.7
0.1562	2.812	0.000209	74.4

[1] These are called basic salts merely because of the excess of alkali in them. Nothing is assumed regarding their constitution.

NEUTRAL POTASSIUM SALT, 5 GRAMS CASEIN+45 CC. N/10 KOH TO 100 CC.

Conc. casein.	$10^6\eta$.	κ_{20}.	$\Lambda = \frac{\kappa}{\eta}$.
5.	45.	0.002430	54.
2.5	22.5	0.001350	60.
1.25	11.25	0.000724	64.4
0.625	5.625	0.000396	70.4
0.3125	2.812	0.000210	74.7
0.1562	1.406	0.000113	80.4

NEUTRAL AMMONIUM SALT, 5 GRAMS CASEIN + 45 CC. N/10 NH_4OH TO 100 CC.

Conc. casein.	$10^6\eta$.	κ_{20}.	$\Lambda = \frac{\kappa}{\eta}$.
5.	45.	0.002167	48.1
2.5	22.5	0.001232	54.8
1.25	11.25	0.000671	59.6
0.625	5.625	0.000355	63.1
0.3125	2.812	0.000191	67.9
0.1562	1.406	0.000103	73.5

NEUTRAL LITHIUM SALT, 5 GRAMS CASEIN + Li_2CO_3 EQUIV. 45 CC. N/10 LiOH TO 100 CC.

Conc. casein.	$10^6\eta$.	κ_{20}.	$\Lambda = \frac{\kappa}{\eta}$.
5.	45.	0.001463	32.5
2.5	22.5	0.000828	36.8
1.25	11.25	0.000461	40.9
0.625	5.625	0.000258	45.8
0.3125	2.812	0.000144	51.2
0.1562	1.406	0.000080	56.2

ACID LITHIUM SALT, 5 GRAMS CASEIN + Li_2CO_3 EQUIV. 22.5 CC. N/10 LiOH TO 100 CC.

Conc. casein.	$10^6\eta$.	κ_{21}.	$\Lambda = \frac{\kappa}{\eta}$.
5.0	22.5	0.000766	34.
2.5	11.25	0.000431	38.3
1.25	5.625	0.000243	43.2
0.625	2.812	0.000133	47.4
0.3125	1.406	0.000071	50.7
0.1562	0.703	0.000038	54.1

Temperature Coefficient.—This was found for a "neutral" casein solution containing in 100 cc. 5 grams of casein and 22.5 cc. N/5 NaOH

at 20° κ=0.001782
27° κ=0.002082

For 1° the difference is 0.00004286 or 2.4 per cent. of the value at 20°. This factor has been used, where necessary, in correcting for all the salts.

Equivalent Conductivity.—It has been suggested by Fuld[1] and more definitely by Laqueur and Sackur[2] that the rapid increase in the Λ values may serve as a measure of the basicity of the casein considered as an acid, following the law first deduced by Ostwald[3] and illustrated by Walden.[4] According to Ostwald the change in the Λ values for monobasic acids is about 10 between the dilutions 32 and 1024 liters and approximately 20, 30, 40 and 50 for the corresponding increasing basicities and same dilution limits. These conclusions are based on the assumption, however, that the acids may be sharply titrated with alkali and phenolphthalein, and that they are fully neutralized. Any conclusions drawn from the behavior of acid salts would lead to inconsistent results, as may be seen by considering the following data from tests with citric and mellitic acids by Walden. I use the true Λ values as given in the Kohlrausch tables[5] rather than the original Walden figures.[6]

Monosodium citrate,	$\Lambda_{1024} - \Lambda_{32}$	.....		41
Disodium	"	"	"	 22
Trisodium	"	"	"	 30
Monosodium mellitate,	"	"	.....	152
Disodium	"	"	"	 65
Trisodium	"	"	"	 65
Tetrasodium	"	"	"	 65
Pentasodium	"	"	"	 67
Hexasodium	"	"	"	 57

While the rule appears to work in some cases it does not in others, and the reason for the failure is not known. Walden himself does not appear to attach importance to it for acid mixtures.

The further suggestion of Laqueur and Sackur to make the relative change in the equivalent conductivity,

$$\frac{\Lambda_{1024} - \Lambda_{32}}{\Lambda_{1024}}$$

[1] Fuld: Loc. cit.
[2] Laqueur and Sackur: Loc. cit.
[3] Ostwald: Z. physik. Chem. **1**, 74; **2**, 901.
[4] Walden: Ibid. **2**, 49, and later papers.
[5] Kohlrausch and Holborn: Work quoted, pp. 170 and 171.
[6] Walden: Z. physik. Chem. **8**, 446.

the measure of basicity gives somewhat more consistent results, but is still of doubtful value when applied to the citrates. The results for the mellitates are a little more regular. From the few casein solutions investigated, Laqueur and Sackur conclude that the casein must be at least tetrabasic, but may be as high as hexabasic, as they find this quotient about 0.33.

The following table shows these relations as calculated from my observations. While they may not have much value in fixing the basicity of the salts they have some value in comparing different kinds of caseins. Λ_B are Λ_A represent the highest and lowest equivalent conductivities respectively; the range of dilution here is the same as from 32 to 1024 liters.

	$\Lambda_B - \Lambda_A$.	$\frac{\Lambda_B - \Lambda_A}{\Lambda_B}$.
Neutral sodium salt	26.2	0.39
" potassium salt	26.4	0.33
" lithium salt	23.7	0.42
" ammonium salt	25.4	0.34
Basic sodium salt	28.3	0.42
" " "	32.0	0.43

As measured by the ratios for mellitic acid the values in the last column suggest a basicity of six. In this connection it will be noticed that the dissociation of some of the salts is nearly complete in the most dilute solutions. In the potassium salt solution the conductivity of the potassium ion would make up about 0.000093 out of 0.000113. The difference is due to the acid ion, which is present in relatively large amount, and possibly to the effect of hydrolysis, slightly. The same thing is essentially true of the neutral sodium salt solution. As the hydrolysis is not very marked, something may be learned by noting the point when, with solutions of increasing alkali content, the effect of the hydroxide in increasing the conductivity becomes apparent. Information additional to that furnished by the phenolphthalein titration may be secured in this way. In the so-called "acid" "neutral" and first "basic" sodium salt solutions the conductivities for equal sodium content are nearly equal, but in the other sodium salt there is a relative increase. A little free hydroxide adds greatly to the conductivity.

OPTICAL ROTATION.

I have already reported the experiments made with casein

from cow's milk[1] and shall merely give the values obtained for comparison.

	$[\alpha]_D^{20}$
Neutral sodium salt	−103.5
Acid sodium salt	− 95.2
First basic sodium salt	−107.6
Second basic sodium salt	−111.8
Neutral potassium salt	−104.4
Neutral lithium salt	−100.8
Acid lithium salt	− 94.8
Neutral ammonium salt	− 97.8

CONDUCTIVITY OF DIGESTIVE MIXTURES.

In the digestion of casein and other proteins with hydrochloric acid and pepsin a number of products are formed which differ with the protein and conditions of experiment. As some of these are basic bodies they combine with the hydrochloric acid and modify the conductivity of the mixtures materially, as has been shown by the experiments of Buzarszky and Liebermann.[2] For a pure product like casein the extent of this modification of the conductivity is somewhat characteristic, as a few experiments which I have already made show. At this time, however, I shall not present any definite figures as the investigation is not complete.

What may be expected in a *prolonged* digestion may be inferred from the following figures. The original potassium salt solution for which $\kappa = 0.00243$ was allowed to stand and undergo spontaneous decomposition, I then found $\kappa = 0.01495$. In this solution the potassium alone should give a value of about 0.0028, from which it is evident that in the breaking down of 5 grams of casein some bodies of considerable conductivity are formed. With the acid lithium salt the result was even more pronounced. The original conductivity was $\kappa = 0.000766$ but after decomposition this had increased to $\kappa = 0.01625$, that is, more than twentyfold. The most strongly basic of the sodium salt solutions, with the original conductivity $\kappa = 0.00382$, was heated twelve hours in a platinum dish on the water-bath and the volume made up to the original. I then found $\kappa = 0.00403$, showing that a slight decomposition had taken place. After standing some weeks, for spontaneous decomposition, I found $\kappa = 0.01177$. A

[1] This Journal, 27, 363.

[2] Buzarszky and Liebermann: Pflüger's Archiv, 72, 51.

marked change is indicated here, but not as much as in the other cases.

In the pepsin-hydrochloric acid digestion with fixed amounts of acid, uniform temperature and constant quality of pepsin, it is possible to control the changes much more perfectly and obtain results of more definite meaning, especially in the comparison of different caseins.

B. CASEIN FROM GOAT'S MILK.

This was prepared essentially as explained for the cow's milk casein, and a good product was obtained, without much difficulty. Dried *in vacuo* over sulphuric acid it held about 2.5 per cent. of water which could be expelled at 105°. In the tests below the vacuum-dried substance was always used, but in amount to correspond to the anhydrous product.

Equivalent Weight.—In these and the following tests enough was weighed out to equal 5 grams of anhydrous casein. It was found by repeated trials that the 5 grams could be dissolved in 42 cc. of N/10 alkali to make a solution neutral to phenolphthalein, both potassium and sodium hydroxides being employed. These results correspond to an equivalent weight of 1190, in place of 1124 as found for the cow's milk casein. This goat milk casein dissolves much more slowly in the alkali than does the other, and the final solution was always more opalescent. As with the casein from cow's milk a solution could be obtained with just half the alkali required to produce neutrality with phenolphthalein.

ELECTRICAL CONDUCTIVITY.

Two solutions only were investigated here; the results are given in the same terms employed for the casein of cow's milk.

NEUTRAL SODIUM SALT, 5 GRAMS CASEIN + 42 CC. N/10 NaOH TO 100 CC.

Conc. casein.	$10^6\eta$.	κ_{20}.	$\Lambda = \frac{\kappa}{\eta}$.
5.00	42.	0.001694	40.3
2.50	21.	0.000942	44.7
1.25	10.5	0.000528	50.3
0.625	5.25	0.000297	56.6
0.3125	2.625	0.000161	61.3
0.1562	1.312	0.000088	67.1

NEUTRAL POTASSIUM SALT, 5 GRAMS CASEIN + 42 CC. N/10 KOH TO 100 CC.

Conc. casein.	$10^6\eta$.	κ_{20}.	$\Lambda = \frac{\kappa}{\eta}$.
5.	42.	0.002219	52.8
2.50	21.	0.001229	58.5
1.25	10.5	0.000665	63.3
0.625	5.25	0.000370	70.5
0.3125	2.625	0.000200	76.4
0.1562	1.312	0.000108	82.3

For both salts the κ values stand below those for the casein from cow's milk, which should be expected from the lower amount of alkali required in combination. The dissociation constants are very nearly the same, however, being 0.40 for the sodium salt and 0.36 for the potassium salt. For the casein from cow's milk they were 0.39 and 0.33 respectively. These observations seem to relate the two kinds of casein.

OPTICAL ROTATION.

On account of the greater opalescence of the goat milk product difficulty was experienced in getting a solution clear enough to read accurately. But this was finally accomplished with the sodium salt and a series of readings were made from which I found:

$$[\alpha]_D^{20} = -105°.$$

The same result was obtained for different solutions of the sodium salt. It is slightly larger than the value for the preparation from cow's milk.

C. CASEIN FROM HUMAN MILK.

As to the real nature of this protein there has always been some doubt. In amount it is far below the casein content of cow's milk and does not make up over 1.5 to 2.0 per cent. of the whole. Relatively large volumes of the milk must therefore be operated upon to secure enough material for satisfactory tests. The experiments I have made in this direction have not, thus far, led to the desired results. The general Hammarsten process of separation is much more difficult of application than with cow's milk, and in addition, the human casein seems to become very readily insoluble in the washing and drying operations. For this reason the salts I have made have not been suitable for accurate conductivity or optical tests, and will not be reported here.

Resumé.—The experiments cited above seem to show only one point of difference between the caseins from cow's and goat's milk and that is in the equivalent weight. The conductivities for equal amounts of alkali are about the same. The greater equivalent weight in the one case may point to the presence of a small additional complex in the casein molecule, or other small group not readily separated in the preparation, which need not exert any effect on the conductivity or rotation. The possibility of such addition groups is often assumed,[1] and would be in keeping with the general character of the casein as a relatively strong acid. But further investigation will be necessary to settle this point.

CHICAGO, December, 1905.

THE SERIES C_nH_{2n-2} IN LOUISIANA PETROLEUM.[2]

BY CHARLES E. COATES.

Received January 11, 1906.

DURING the last three years, I have had occasion to examine, with some care, samples of oil from the various Louisiana oil fields. The results of these investigations showed that the oils were of an asphaltic base, with lighter hydrocarbons of the series C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}, etc. These series had already been isolated by Mabery, Richardson and others. The various members were saturated, or at least did not add bromine, and had molecular refractions which did not indicate a double union. As the lowest member of this series C_nH_{2n-2} then known was $C_{12}H_{22}$, Mabery suggested that it was dihexahydrodiphenyl and the remaining members were its homologues. This formula seemed to agree with all the properties of these hydrocarbons and was accepted by Richardson in his recent book on the "Asphalt Pavement."

When, however, I began the examination of the crude oil from Jennings, which is the lightest of any of the Louisiana petroleums, I found that there was a small quantity of the very lightest fraction obtained by distillation which gave a molecular weight considerably too low for $C_{12}H_{22}$. From about ten gallons of the crude oil I obtained about 25 cc. of the new fraction in a fair state of purity, and found it to have the formula $C_{11}H_{20}$, and to

[1] See, for example, Raudnitz: Ergebnisse der Physiologie, **2**, 217.

[2] Read at the New Orleans Meeting of the American Chemical Society.

possess to a marked degree the odor of turpentine. Moreover, there was a small quantity of a still lighter oil obtained but not enough for analysis. As $C_{11}H_{20}$ can not be derived from dihexahydrodiphenyl, $C_{12}H_{22}$, I undertook the study of these lighter fractions and, as a preliminary step, I endeavored to prepare them in a state of purity and in some quantity. The amount in the crude oil is very little, but through the courtesy of Mr. Alba Heywood I obtained about five gallons of the first distillate from the Jennings refinery, which I found to consist mainly of hydrocarbons of from C_{13} upwards, but to contain enough of the lower members to give a fair amount of $C_{10}H_{18}$, $C_{11}H_{20}$ and $C_{12}H_{22}$. These substances possessed the turpentine odor, which was faint immediately after distillation and became stronger after the flask was allowed to stand uncorked for several days.

It proved exceedingly difficult to get the new members of this series in a state of purity. Indeed, I do not think it can be done by fractional distillation. $C_{11}H_{20}$ boils at about 190–200°, at 60 mm. Possibly a liter of this fraction was collected and purified as usual with fuming sulphuric acid and sodium hydroxide. The resulting oil was clear and water-white, but upon redistillation it broke up into fractions boiling from 180° to 210° and leaving a yellow residue. There had evidently been decomposition, but nevertheless a series of fractional distillations at 760 mm. was instituted. Several hundred distillations were made, but each fraction continued to break up into fractions with a lower and a higher boiling-point, the latter yielding considerable tarry matter to fuming sulphuric acid. In no case could a constant boiling-point be obtained.

In order to determine the effect of heating, a water-white fraction collected from 215° to 220°, corresponding to the substance $C_{12}H_{22}$, was boiled for twenty-four hours with a return condenser. It turned yellow but on distillation gave fractions from 205° to 230°, which was about what the original oil would have done, though possibly there was a larger amount of the higher fractions than usual. Next, a long copper tube was heated to redness for two feet and the remaining portion was cooled by water. A flask was fitted into the hot end with an asbestos stopper and the 215–220° fraction was distilled slowly through the tube. There was much decomposition and the issuing oil was dark and thick, yielding to fuming sulphuric acid at least

half its volume, a tarry mass being formed. The purified oil, however, boiled at about the same temperature as the original and had about the same physical constants. Evidently superheating and sudden cooling had brought about condensation of a considerable portion of the oil to a semi-asphaltic mass, the remainder being unaffected because it had probably escaped superheating in its passage through the tube.

Distillation under diminished pressure gave less decomposition than at 760 mm., but even at 16 mm. there was some decomposition. I made several hundred distillations at from 16 mm. to 30 mm., but still could not obtain a substance of constant boiling-point. For example, a fraction boiling at 80–85° at 30 mm., was distilled fractionally at least fifty times, at the end of which, the fraction collected from 80–82° gave, on redistillation at 30 mm., fractions from 75° to 90°, these having different specific gravities, etc. Though these yielded considerable tarry matter to fuming sulphuric acid, the resulting oil was not very different from the oil before treatment. A fraction having sp. gr. $0.8199^{25}/_{4}$, molecular weight 139, N_D^{25} 1.4470, gave, after the acid treatment, 0.8197, 142 and 1.4472 respectively.

As the apparent boiling-point did not appear to be an exact index as to the nature of the distillates, these were collected and united according to their refractive indices, but the results were no better. Finally all the available material was fractionated at 760 mm., purified, refractionated, repurified, and then fractionated at 21 mm. a large number of times, using a Glinsky tube.

A series of distillates were eventually obtained which, at 21 mm., boiled inside a range of 5°, the major portions coming over in the middle 2°. The molecular weight of each fraction was determined and those fractions which corresponded to the theoretical formula were taken as representing the corresponding hydrocarbon in a state of as great purity as I was able to obtain. The refractive index, specific gravity and boiling-point at 760 mm. were next determined, then the combustion was made. The results are given in a tabulated form below.

Formula.	Molecular weight calculated.	Molecular weight found.	Carbon calculated.	Carbon found.	Hydrogen calculated.	Hydrogen found.	Sp. gr.	B. P. at 760 mm.	N_D^{25}	Molecular refraction calculated.	Molecular refraction found.
$C_{10}H_{18}$,	138	138	86.95	86.81	13.05	13.01	$0.8146^{22}/_{4}$	168–70	1.4460	43.92	44.96
$C_{11}H_{20}$,	152	151	86.84	87.00	13.16	12.88	$0.8378^{28}/_{4}$	198–200	1.4582	48.53	48.76
$C_{12}H_{22}$,	166	167	86.74	86.68	13.26	13.43	$0.8511^{28}/_{4}$	215–7	1.4640	53.13	53.48
$C_{13}H_{24}$,	180	181	86.67	86.58	13.33	13.42	$0.8629^{22}/_{4}$	235–8	1.4692	57.73	57.93

This table gives only the members from C_{10} to C_{13}. I hope to be able to supply the deficiencies and to complete the purification of C_{14} to C_{17} inside of the next few months. I might add, as to the figures given, that in each case the same hydrocarbon was prepared from fresh material some six or eight times and as the results were concordant they might be taken as fairly well established. I also obtained two fractions with the following constants:

	Mol. wt.	Sp. gr.	N_D^{25}.	B. P.	Quantity.
[C_9H_{14} = 110]	111	$7747^{24}/_{4}$	1.4260	120.5	about 3 cc.
[C_9H_{18} = 124]	124	$7992^{24}/_{4}$	1.4370	145.7	about 5 cc.

These substances were present in such small quantity that they could not be purified. A combustion of the second gave results between those for C_9H_{18} and C_9H_{22}. The first was not burned.

I have done very little so far as to determining the purely chemical properties of the oils. The smell of turpentine suggested optical activity, but they were all inactive. Tested with a Hübl and a Harms iodine solution and with an ethereal solution of bromine, there was not the slightest evidence of unsaturation of the ordinary type. Neither have I been able to fit the hydrocarbons into any series of known constitutional formula. Take $C_{10}H_{18}$ for example, which I purified with particular care. It was inactive and saturated. Being saturated it must belong to a cyclic series, but there is exceedingly little literature on the cyclic series C_nH_{2n-2} and what there is, is rather vague. The various menthenes, hydrocamphenes, etc., have physical properties not far off from those of this $C_{10}H_{18}$, but they add bromine, mostly, and are generally optically active. A methylbicyclononane[1] has general properties which correspond fairly well with those of $C_{10}H_{18}$, but the specific gravity is a little too high ($0.8416^{20}/_{4}$).

[1] Ber. 37, 1674.

However, an isopropylmethylbicyclononane[1] corresponds almost exactly with the new $C_{13}H_{24}$, the constants being, sp. gr. $0.8645^{20}/_{4}$; N_D 1.4660. The homologue of tetrahydrobenzene, $C_{10}H_{18}$, would probably add bromine, though this is perhaps doubtful, but it would show a double union, which is not indicated by the molecular refractions in the series under discussion. All things considered, a bicyclic formula seems the most probable, but as yet the data do not permit of a definite determination of this point. It does seem clear, however, that we have here a homologous series beginning at least as low as $C_{10}H_{18}$. This would make the dihexahydrodiphenyl theory proposed by Mabery and by Richardson untenable. The question is of considerable interest for there is undoubtedly a connection of some sort between this series and asphaltum, and despite the importance of asphaltum, we know almost nothing of its chemical composition. I hope to continue the study of the lower members, C_9 to C_{12}, as soon as I am able to purify enough to work with.

CONTRIBUTION FROM THE U. S. DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY, No. 59. SENT BY H. W. WILEY.]

AMERICAN COD LIVER OILS.[2]

BY L. M. TOLMAN.

Received December 28, 1905.

A STUDY of American cod liver oils was begun about a year ago by the Bureau of Chemistry of the United States Department of Agriculture, with the coöperation of the United States Bureau of Fisheries. The facilities of the Bureau of Fisheries, and especially the coöperation of Dr. H. M. Smith, has enabled us to obtain for our study a collection of fish liver oils which are of extraordinary interest and value in the following particulars: First, the large number and variety of the oils obtained; second, the data regarding the source and history of the samples; third, the oils were prepared from the fish as soon as they were caught, thus assuring oils which had undergone no decomposition; and fourth, the condition of the fish from which the oil was prepared was carefully noted. This last condition is of special importance,

[1] Ber. 37, 1666.

[2] Read before the Lewis and Clark Pharmaceutical Congress, Portland, Oregon, 1905.

as it explains, to a certain degree, the extraordinary variation in composition of oils from the same variety of fish.

This investigation was begun at the suggestion of Mr. L. F. Kebler, chief of the Drug Laboratory of the Bureau of Chemistry, and the work has been done in collaboration with him. The primary object of the investigation was to make a thorough study of American cod liver oils to find if they differed in any way from Norwegian oils, and whether the difference in market price was due to any actual difference in value or only to the reputation of the Norwegian article.

The investigation includes a study of the chemical composition of the oils, the methods and conditions of manufacture, and the condition of the fish used, as well as a comparative test of the actual medicinal value of the different oils. A number of other objects of no less importance were, however, in mind, such as the study of methods for the detection of adulteration, which in recent years has probably increased, owing to the scarcity and accompanying high price of pure cod liver oil; a study of the other fish liver oils to see if they differ from cod liver in chemical composition or in medicinal value; and finally, an examination of the tests required by the U. S. Pharmacopoeia to see if pure American cod liver oils can conform to the requirements to which they will be subjected.

The latter investigation, which is perhaps as important as any to the American producer, will be the subject of this article, including, however, a discussion of the value of these tests as a criterion of purity. The tests as laid down in the U. S. Pharmacopoeia are based on the reactions and composition of Norwegian oils, and the difference in conditions of production and manufacture in this country might affect many of the purely qualitative reactions which are often due to substances which in no way affect the quality or value of the oil. Especially is this true of the numerous color tests, which of late have fallen into bad repute not only in this country but in England, where a number of cases have occurred in which they have proved of little or no value in judging of purity.

The cod liver oils examined were twenty-one samples furnished the Bureau of Fisheries; two Alaskan oils of undoubted purity, four Newfoundland oils obtained by the American consul at St. Johns, three samples of Norwegian oils obtained by the American

consul at Bergen, ten commercial Norwegian oils taken from the original packages in which they were imported, by the United States custom officials, and two commercial American oils.

The cod liver oils supplied by the Bureau of Fisheries were prepared from fish caught at different seasons of the year and on different fishing grounds, and so represent the extremes of variation liable to occur in oil. They were from fat fish caught early in the fall long before the spawning season, and from fish taken just before, during, and after the spawning season, and the results show that the composition of the oil varies to an extraordinary degree, depending on the condition of the fish.

These variations are much wider than obtains with the Norwegian product, which is prepared from fish caught in a very short season and which are in about the same condition. This means that one may expect that constants and tests based on Norwegian oils will not be satisfactory when applied to the American oils, and it would be unjust to the American producer to compel him to comply with them. Especial attention was called to this fact by an American producer who was unable to place upon the market a medicinal oil of undoubted purity and of a high grade because it failed to respond to one of the color tests prescribed.

Beside the cod liver oils a number of other fish liver oils were obtained for comparison. These are the oils most likely to be used as adulterants. The list of other fish liver oils[1] examined is as follows:

Cusk, *Brosmius brosme* (Müller); Hake, *Urophycis tenius* (Mitchell) and *Urophycis chuss* (Walbaum); Haddock, *Melanogrammus aeglifinus* (Linnaeus); Pollock, *Pollachius virens* (Linnaeus); Sunfish, *Mola mola* (Linnaeus); Dogfish, *Squalus acanthius* (Linnaeus).

The oils from the above-named fish were furnished by the Bureau of Fisheries, having been prepared from fish freshly caught and all the data as to the condition of the fish, etc., recorded. Two samples of Norwegian fish liver oils liable to be used as adulterants of cod liver oil were obtained by the American consul at Bergen, namely, coal fish, *Pollachius virens* (Linnaeus)

[1] The writer is in debt to Barton W. Evermann, of the Bureau of Fisheries, for the scientific names of the different fish.

the same as the pollock, and ling, *Brosmius brosme*, the same as the cusk.

The U. S. Pharmacopoeia requires that the oil must have a specific gravity of 0.918–0.922 at 25° C. The following table shows the determinations made on twenty American oils:

AMERICAN COD LIVER OILS.

Serial number.	Sp. gr. at 15.5° C. / 15.5° C.	Sp. gr. at 25° C / 25° C.	Index of refraction 15.5° C.	Iodine number.
14273	0.9224	0.9174	1.4783	135.4
11307	0.9230	0.9180	1.4783	135.5
11372	0.9232	0.9182	1.4795	144.4
11302	0.9232	0.9182	1.4796	147.8
11274	0.9239	0.9189	1.4801	145.4
11275	0.9245	0.9195	1.4805	152.4
14305	0.9245	0.9195	1.4801	150.4
14309	0.9246	0.9196	1.4802	152.9
14308	0.9248	0.9198	1.4802	153.6
14306	0.9249	0.9199	1.4806	154.1
14326	0.9250	0.9200	....	....
14310	0.9251	0.9201	1.4806	157.8
14303	0.9254	0.9204	1.4812	158.2
11271	0.9256	0.9206	1.4806	157.3
14263	0.9260	0.9210	1.4814	162.5
14327	0.9265	0.9215	....	....
14324	0.9265	0.9215	....	....
14325	0.9266	0.9216	....	....
14272	0.9268	0.9218	1.4803	157.7
11596	0.9270	0.9220	1.4814	172.6

This table shows that only one out of the twenty samples examined was below the minimum allowed, which would indicate that the limits set are satisfactory for American cod liver oil, although other oils may show wider variation.

Little value can be placed on this determination as separating or indicating mixtures of other fish liver oils, as can be seen when it is noted that all the other oils come within these limits with the exception of dogfish liver oil, additions of which might easily be detected by the low specific gravity and index of refraction.

QUALITATIVE TESTS OF THE PHARMACOPOEIA.

Test No. 1.—"If one drop of the oil be dissolved in 20 drops of chloroform and the solution shaken with one drop of sulphuric acid, the solution will acquire a violet-red tint, rapidly changing to rose-red and finally to brownish yellow."

It is the experience of the author that the colors obtained depend to a great extent on the size of the drop of sulphuric acid added. If a small drop is added, the change of colors is comparatively slow, and one obtains at first instead of the violet-red a beautiful blue and then a violet-red and finally a red or reddish brown.

If, however, a large drop is added the change of colors is so rapid that the blue color is hardly apparent, the violet-red developing almost instantly, and at no stage does the rose-red color, which shows so beautifully in the nitric acid test, develop.

If carbon bisulphide is used as the solvent instead of chloroform, as described by the German Pharmacopoeia, the blue color does not develop and we have a red-violet changing almost at once into a brown. This test, however, is unfortunately given by all fish liver oils. The author applied the test to all the fish liver oils used in this work and found that they gave identical results, so that this test is of no value in identifying cod liver oil as distinguished from the other fish liver oils. Even the oil from the liver of the dogfish, a species of shark, gives this test. It was also found that cod liver oils which had been exposed to the action of light and air for a considerable time give instead of the blue only a reddish color.

Test No. 2.—"If a glass rod moistened with sulphuric acid be drawn through a few drops of the oil on a porcelain plate, a violet color will be produced."

This color reaction is undoubtedly due to the presence of the same substance which produces the blue-violet color in the previous test and has the same value and the same limitations. All the fish liver oils gave this test in just as marked a manner as cod liver oil, and the oils which had been exposed to the light and air and failed to give the other test failed also when this test was applied.

Test No. 3.—"If 2-3 drops of fuming nitric acid be allowed to flow along side of 10–15 drops of the oil contained in a watch-glass, a red color will be produced at the point of contact. On stirring the mixture with a glass rod the color becomes a bright rose-red, changing to a lemon-yellow. (Distinction from seal oil, which shows at first no change of color, and from other fish oils, which become at first blue and afterwards brown and yellow.)"

This is known as the nitric acid test and has been considered the

		Acid sp. gr. 1.40.		
		Color developed at once.	Color developed on standing half hour.	
2447	High-grade Norwegian oil	Red to rose-red.	Lemon-yellow.	Red to rose
11226	Alaskan cod liver oils, high grade	Little color.	Brown.	Purple at po
11227	Alaskan cod liver oils, high grade	Brownish.	Brown.	Purple at po
11337	Newfoundland cod liver oils, American consul at St. Johns..	Little color.	Brown.	Brownish r
11338	Newfoundland cod liver oils, American consul at St. Johns..	Red to rose-red.	Lemon-yellow.	Red to rose
11339	Newfoundland cod liver oils, American consul at St. Johns..	Red to brown.	Brown-red.	Red to rose
11340	Newfoundland cod liver oils, American consul at St. Johns..	Red to rose-red.	Orange.	Red to rose
11372	American cod liver oil from U. S. Bureau Fisheries	Slight red.		Purple at p
11596	American cod liver oil from U. S. Bureau Fisheries	Red to rose-red.	Yellow.	Red to rose
14273	American cod liver oil from U. S. Bureau Fisheries	Red to rose-red.	Red.	Purple at p
14274	American cod liver oil from U. S. Bureau Fisheries	Red to rose-red.	Deep brown.	Purple at p
14275	American cod liver oil from U. S. Bureau Fisheries	Red to rose-red.	Brown.	Purple at p
14302	American cod liver oil from U. S. Bureau Fisheries	———	———	Purple at p
14303	American cod liver oil from U. S. Bureau Fisheries	———	———	Purple at p
14305	American cod liver oil from U. S. Bureau Fisheries	———	———	Purple at p
14306	American cod liver oil from U. S. Bureau Fisheries	———	———	
14307	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose
14308	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose
14309	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose
14310	American cod liver oil from U. S. Bureau Fisheries	———	———	Purple to r
14324	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose
14325	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose
14326	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose
14327	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose
11371	American hake liver oil from U. S. Bureau Fisheries	Slight reddish.	Yellow.	Purple at p
11373	American cusk liver oil from U. S. Bureau Fisheries	Slight reddish.	Yellow-brown.	Slight red
11376	American sunfish liver oil from U. S. Bureau Fisheries	Red to rose-red.	Yellow.	Red to rose
11594	American pollock liver oil from U. S. Bureau Fisheries	Red to rose-red.	Yellow.	Red to rose
11595	American haddock liver oil from U. S. Bureau Fisheries	Red to rose-red.	Red-brown.	Red to rose
11597	American dogfish liver oil from U. S. Bureau Fisheries	No action.	Brown.	Brown.
11556	Norwegian ling liver oil from American consul at Bergen	Red to rose-red.	Yellow.	Red to rose
11557	Norwegian coalfish liver oil from American consul at Bergen	Red to rose-red.	Yellow.	Red to rose

COLOR REACTIONS OF FISH LIVER OILS WITH NITRIC ACID OF DIFFERENT STRENG

Acid sp. gr. 1.40.		Acid sp. gr. 1.46.	
Color developed at once.	Color developed on standing half hour.	Color developed at once.	Color develop standing hal
Red to rose-red.	Lemon-yellow.	Red to rose-red.	Lemon-yell
Little color.	Brown.	Purple at point of contact, changing to brown.	Deep brown
Brownish.	Brown.	Purple at point of contact, changing to brown.	Brown.
Little color.	Brown.	Brownish red.	Orange.
Red to rose-red.	Lemon-yellow.	Red to rose-red.	Yellow.
Red to brown.	Brown-red.	Red to rose-red.	Yellow.
Red to rose-red.	Orange.	Red to rose-red.	Yellow.
Slight red.		Purple at point of contact, changing to red.	Yellowish b
Red to rose-red.	Yellow.	Red to rose-red.	Yellow.
Red to rose-red.	Red.	Purple at point of contact, changing to red.	Yellow.
Red to rose-red.	Deep brown.	Purple at point of contact, changing to red.	Brown.
Red to rose-red.	Brown.	Purple at point of contact, changing to red.	Brown.
———	———	Purple at point of contact, changing to red.	Brown.
———	———	Purple at point of contact, changing to red.	Black.
———	———	Purple at point of contact, changing to red.	Yellow.
———	———		Yellowish b
———	———	Red to rose-red.	Yellowish b
———	———	Red to rose-red.	Yellowish b
———	———	Red to rose-red.	Yellowish b
———	———	Purple to rose-red.	Yellowish.
———	———	Red to rose-red.	Yellow.
———	———	Red to rose-red.	Yellow.
———	———	Red to rose-red.	Yellow.
———	———	Red to rose-red.	Yellow.
Slight reddish.	Yellow.	Purple at point of contact, changing to red.	Yellow.
Slight reddish.	Yellow-brown.	Slight red, changing to rose-red.	Reddish bro
Red to rose-red.	Yellow.	Red to rose-red.	Yellow.
Red to rose-red.	Yellow.	Red to rose-red.	Yellow.
Red to rose-red.	Red-brown.	Red to rose-red.	Reddish bro
No action.	Brown.	Brown.	Brown.
Red to rose-red.	Yellow.	Red to rose-red.	Yellow.
Red to rose-red.	Yellow.	Red to rose-red.	Yellow.

	Acid sp. gr. 1.49.	
Color developed on standing half hour.	Color developed at once.	Color developed on standing half hour.
Lemon-yellow.	Purple at point of contact, changing to rose-red.	Lemon-yellow.
Deep brown.	Very strong purple, changing to red and brown.	Black.
Brown.	Very strong purple, changing to red and brown.	Black.
Orange.	Purple at point of contact, changing to red-brown.	Brownish yellow.
Yellow.	Purple at point of contact, changing to red.	Yellow.
Yellow.	Purple at point of contact, changing to red.	Orange.
Yellow.	Purple at point of contact, changing to red.	Orange-yellow.
Yellowish brown.	Strong purple, changing to red.	Orange.
Yellow.	Purple to rose-red.	Yellow.
Yellow.	Purple to rose-red.	Yellow.
Brown.	Purple to rose-red.	Blackish.
Brown.	Purple to rose-red.	Brown.
Brown.	Deep purple to red.	Black.
Black.	Deep purple to red.	Black.
Yellow.	Deep purple to red.	Dark brown.
Yellowish brown.	Deep purple to red.	Orange.
Yellowish brown.	Deep purple to red.	Yellow-brown.
Yellowish brown.	Deep purple to red.	Yellow-brown.
Yellowish brown.	Deep purple to red.	Yellow-brown.
Yellowish.	Deep purple to red.	Orange.
Yellow.	Deep purple to red.	Yellow.
Yellow.	Deep purple to red.	Yellow.
Yellow.	Deep purple to red.	Yellow.
Yellow.	Deep purple to red.	Yellow.
Yellow.	Deep purple to red.	Orange-yellow.
Reddish brown.	Purple, changing to red and brown.	Brown.
Yellow.	Deep red.	Orange.
Yellow.	Purple to rose-red.	Yellow.
Reddish brown.	Purple to red.	Red-brown.
Brown.	Purple to brown.	Brown.
Yellow.	Purple to rose-red.	Yellow.
Yellow.	Purple to rose-red.	Yellow.

best test for cod liver oil and is used to a greater extent than any other.

The author has found that a great difference in the test is brought about by the variation in strength of the fuming nitric acid used. A series of experiments was made on the various oils with acids of different strength. Three acids were used: First, ordinary acid, sp. gr. 1.40; second, fuming acid, sp. gr. 1.46; and third, fuming acid, sp. gr. 1.49. The acid of sp. gr. 1.40 was evidently too weak to be satisfactory, although it gave the characteristic rose-red with many of the oils, but with some of the oils it failed to react.

The preceding table shows the difference of color produced by the different acids:

The first oil in the table is a high-grade Norwegian oil and the test as applied to it is typical, the results agreeing exactly with the description given in the method of the colors formed and the different changes in color during the reaction. All the Norwegian oils examined reacted in very much the same manner. The only point, however, to be noted with this sample is the fact that with the fuming acid, sp. gr. 1.49, instead of a red color being produced at the point of contact between the acid and oil a purple color is developed. This, however, quickly changes to red and rose-red and finally to yellow, but when the American oils are examined a very different condition is noted. Very few give the marked typical reaction given by the Norwegian oil. The two Alaskan oils gave with the acid sp. gr. 1.46 a purple color which changed to brown on standing, and in fact a considerable proportion of the American oils gave a brown color on standing.

There seems to be more of the substance present in American oils which gives the blue color with nitric acid. This is shown by the fact that nearly all give a purple color at the point of contact between the oil and the acid with the acid sp. gr. 1.46, while none of the Norwegian oils gives this color with this strength of acid. However, with stronger acid, sp. gr. 1.49, most of the Norwegian oils showed the purple at the point of contact.

The color obtained is practically the same in all cases except in quantity, rose-red being a mixture of blue and red, while purple is also a mixture of these same colors but in different proportions. The most important point, however, to be noted is the brown color which develops in so many of these oils, which,

according to the last section of the method, would classify them as "other fish oils."

There is a question, however, as to what is meant by the phrase "other fish oils." Probably other fish *liver* oils, as the fish oils, such as menhaden and herring do not give the blue color so characteristic of the liver oils. In fact this nitric acid test is a general test for fish liver oils and is coming to be so considered and not as a specific test for cod liver oil, as will be seen from the reactions given by the other fish liver oils shown in the table. Hake, pollock, haddock, ling, coalfish, and cusk liver oils give reactions which can in no way be distinguished from cod liver oil. Even dogfish liver oil gives the reaction, although not quite so strongly.

From these results, therefore, practically all that we can say is that this is a test for fish liver oils and should be given by cod liver oil, but that American oils do not react exactly like Norwegian oils, giving often a purple color changing into a brownish yellow. Also the strength of the fuming nitric acid used makes a great difference with the colors produced.

Another point which must be taken into consideration is the age of the oil and the conditions to which it has been exposed. Oils which have been exposed to light and air do not react as strongly as fresh oils and in some cases fail entirely, but this only takes place when the oil has been very badly treated. Some experiments made, allowing oils to stand in the light in tightly corked bottles for nearly a year, showed that the color reactions of the oil were not affected. When, however, the same oil was exposed in an uncorked bottle for a much shorter time it was very much changed and failed to give the proper color tests. Oils which are properly handled should give the proper tests after long standing.

The range of iodine number of 140–150 as given in the Pharmacopoeia seems to be exceedingly narrow. The method for the determination of iodine number given by the U. S. Pharmacopoeia has been largely abandoned of late because of the rapid change which a mixture of the test solutions of alcoholic iodine and alcoholic mercuric chloride undergoes in the first few hours. Under the conditions of the analysis the blank determination is liable to greater change on account of the larger amount of iodine present, and results obtained by this method are lower than they should be.

The Hanus solution, iodine monobromide, dissolved in glacial acetic acid, has many advantages as a reagent in this determination on account of its stability and permanence. Using this solution for determining the iodine number of the cod liver oils examined, a much wider variation was found than is suggested in the U. S. Pharmacopoeia. This is due, however, to the same reason as was noted in the discussion of the variation observed for the specific gravity and other constants.

In conclusion, the writer would say that the standards and tests of the U. S. Pharmacopoeia which are satisfactory for Norwegian oils are not applicable to the American oils, which are liable to show more variation, and the color tests as laid down are not characteristic of cod liver oil but only of fish liver oils. Further, the nitric acid test is liable to give misleading results with many pure cod liver oils of American origin.

THE PREPARATION OF ALDEHYDE-FREE ETHYL ALCOHOL FOR USE IN OIL AND FAT ANALYSIS.

By Frederick L. Dunlap.

Received January 2, 1906.

One of the most common reagents in the analysis of oils and fats is alcoholic potassium hydroxide. In the preparation of this reagent, it is necessary to remove the aldehyde from the alcohol before the potassium hydroxide is dissolved in it, otherwise the solution obtained is more or less dark colored, according to the amount of aldehyde present. There are cases in which the dark color of the alcoholic potassium hydroxide offers no obstacle, but where the solution is a standard, it is necessary that it be water-white. Especially is this true where a titration is made in a solution which is itself dark colored and in which the end-point is, at best, not of the sharpest. Cases of this kind are by no means infrequent in determining the saponification value of oils and fats.

In the preparation of aldehyde-free alcohol, it is desirable that the method be fairly rapid, and that the yield be as nearly quantitative as possible. The most common method is to treat the alcohol with potassium hydroxide (10 grams per liter) and let stand for ten days to two weeks; or, in lieu of this, to boil this alcoholic solution for three hours. The dark colored solution

is then distilled and the distillate used in the preparation of the alcoholic potassium hydroxide. It has been my experience that under the conditions as given, the acetaldehyde is not completely resinified and that the first fractions must be rejected. In fact, I have found the same to be true in cases where much more than 10 grams of potassium hydroxide were added to each liter of alcohol and where such solutions stood for several months before distillation.

Waller[1] has proposed the treatment of alcohol with potassium permanganate, letting the solution stand until the permanganate has all been reduced and then fractioning with a column, rejecting those fractions which turn yellow with potassium hydroxide. This method is, at best, a slow one, as the fractioning is to be conducted so that no more than 50 cc. of distillate are obtained in twenty minutes. Then too, the yield of aldehyde-free alcohol is reduced by the amount that must be rejected on account of its turning yellow with alkali.

Bell[2] has suggested a method in which 500 cc. of alcohol are treated with 25 grams of potassium hydroxide and the resulting solution boiled with 250 grams of lard or other easily saponifiable fat, after which the alcohol is distilled from the resulting soap and unsaponified oil and used for preparing alcoholic potassium hydroxide solutions. Bell states that he obtains 450 cc. of good alcohol by this process.

Kitt[3] has objected to Waller's method on the ground of the yield, and has suggested that better results may be obtained by fractioning the alcohol without the use of potassium permanganate, rejecting those portions that turn yellow with potassium hydroxide. I may say that Kitt's method likewise may be reasonably objected to on the same ground that Kitt objected to Waller's. For example, I found that a sample of commercial 95 per cent. alcohol on fractioning gave but 40–50 per cent. of an aldehyde-free product, whereas if a column was used the yield was increased to 75 per cent., yet this is far from satisfactory.

In a recent article in the Berichte,[4] L. W. Winkler gives a method for preparing pure absolute ethyl alcohol, in which the

[1] This Journal, 11, 124 (1889).
[2] J. Soc. Chem. Ind. 12, 236 (1893).
[3] Chem. Rev. Fett Harz Ind. 11, 173 (1904).
[4] Ber. 28, 3612 (1905).

aldehyde is removed by means of silver oxide. Winkler prepared the silver oxide by precipitating silver nitrate with an excess of alkali, washing, and drying at ordinary temperatures. In order to make the silver oxide as effective as possible, it must be finely divided, so Winkler was obliged to grind the dry silver oxide in a mortar with a small amount of alcohol before adding it to the main lot which was to be purified. The alcohol and oxide were allowed to stand for several days with frequent shaking. The alcohol so treated was found to be absolutely aldehyde-free.

The above method of Winkler suggested to me the use of silver oxide in preparing aldehyde-free alcohol for use in oil and fat analysis and, with certain variations, gave a method which leaves little to be desired so far as ease of execution, rapidity, and yield are concerned. The principal variation from Winkler's method lies in the fact that the silver oxide is precipitated *in* the alcohol, in a finely divided condition, being therefore more active and rapid in its action than when prepared apart and then added. The method I have adopted is as follows:

Dissolve 1.5 grams of silver nitrate in about 3 cc. of water and add it to a liter of 95 per cent. alcohol in a glass-stoppered cylinder, then mix thoroughly. Dissolve 3 grams of potassium hydroxide (by alcohol) in 10 to 15 cc. of warm alcohol and, after cooling, pour it slowly into the alcoholic silver nitrate solution, but do not shake. The silver oxide is precipitated in a very finely divided condition and slowly distributes itself throughout the contents of the cylinder. Let stand quietly over night or until the precipitated silver oxide has completely settled. Either siphon off the clear supernatant liquid from the sediment or filter, and distil. None of the distillate need be rejected for it will all give with potassium hydroxide a water-white solution. Moreover, due to the excess of alkali used, the distillate is perfectly neutral and therefore serviceable for the determination of the acid value of oils, or for any other purpose where a neutral alcohol is necessary.

The amount of silver nitrate given in the method above may or may not furnish sufficient silver oxide for rapid and complete oxidation of the aldehyde, for this will depend on the amount of aldehyde in the alcohol treated, but the amount of silver nitrate may be varied to suit the need for it. However, the proportions

given have proved ample for any alcohol which I have had occasion as yet to make aldehyde-free.

If for any reason it may be desirable to avoid the use of water in dissolving the silver nitrate, this salt may be powdered and then dissolved in the 95 per cent. alcohol, and then the alkali added to this.

The above method has several advantages over the procedure of Winkler. There is a great saving of time in precipitating the silver oxide in the alcohol rather than preparing it apart and then utilizing it. The great advantage gained by this is that the oxide is thrown down in such a minute state of subdivision and hence in the very best condition for a rapid and complete oxidation of the aldehyde. If the cylinder be shaken after the addition of the alkali, the silver oxide gathers in flocks which rapidly settle to the bottom of the cylinder, and are thus much less effective than the finely divided and slowly settling precipitate. Shaking is therefore to be avoided.

It should be said in justice to Winkler, that the method outlined above would have been impracticable for his purpose, for he was preparing pure absolute alcohol and the introduction of water into the so-called absolute alcohol which he used as his starting point would not have been feasible. Furthermore, silver nitrate is practically insoluble in absolute alcohol so that it was necessary to prepare the silver oxide separately. For fat analysis, the presence of a few per cent. of water in the alcohol offers no disadvantages.

The method as outlined above is not applicable to methyl alcohol.

I wish to thank Mr. Lorin H. Bailey for his aid in carrying out a part of the experimental work on this subject.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
December 27, 1905.

NOTES.

Note on the Condensation of Succinylosuccinic Esters with Amidines.—In a recent paper in this Journal (**27**, 1302) by us, the condensation of succinylosuccinic acid diethyl ester with acetamidine and the product resulting therefrom are described. Before this work was undertaken the literature was examined

to discover whether this reaction had been previously investigated, and finding no record of the kind we assumed that it had not. We find, however, that our search of the literature was not sufficiently thorough, for Prof. Dr. A. Pinner, of Berlin, has called our attention to the fact that he carried out the same reaction many years ago with benzamidine[1] and obtained an analogous product. Pinner called his product a "dihydrodiphenyldioxy*antetrazin*," while we described ours as a "dihydrodimethyldihydroxy-*naphtotetrazine*," following in this name the nomenclature adopted for such heterocycles by Richter's Lexikon.

In comparing Pinner's diphenyl derivative with our dimethyl derivative, it is interesting to note that he assigns a similar structure to his product, and that in general the two compounds behave similarly. Both are insoluble in practically all solvents except the caustic alkalies, and are very inert. Both form well crystallized sodium salts; that of the diphenyl derivative carries four molecules of water, while ours carries six.

We wish to make this apology to Prof. Pinner for having overlooked his work, and hope that he may find something of interest in the results secured by us, which corroborate and extend the reaction which he was the first to investigate.

M. T. BOGERT AND A. W. DOX.

COLUMBIA UNIVERSITY, January 19, 1906.

Blast-lamp for Gasoline or City Gas.—The writer has designed the burner shown in this drawing and while no claim whatsoever is made to any originality, he thinks he may confer a favor in describing it to iron and steel chemists who have had some trouble in obtaining a good blast-lamp and who require a high temperature burner at a greatly reduced cost. All the materials required are $\frac{3}{4}$-inch tee, $\frac{3}{4}$-inch pipe, $\frac{1}{8}$-inch pipe and plugs of brass. They are assembled as shown. The wooden block shown in Fig. 2 is the support for the burner. It can be secured to the laboratory desk by a rod and tap, a hole being bored through the center of the block. This gives perfect rigidity with enough play to get the burner directed at any convenient angle. The air pipe is usually reduced to various sizes of capillary bore, from 1/64 inch up. This, of course, must be determined by the pressure of air available and the kind of work the

[1] Ber. 22, 2625.

burner is required to perform. In this laboratory I have six in use giving anywhere from a brush flame 20 inches high to a fine "hat

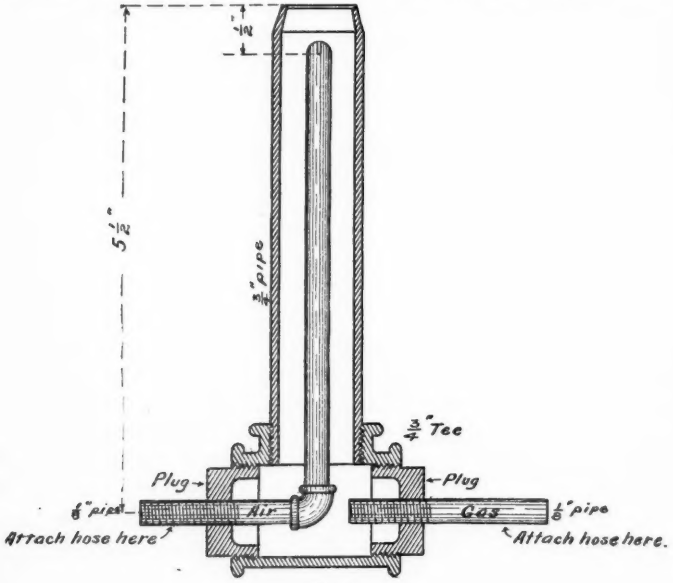

Fig. 1.

pin" flame. The air supply is compressed air at 80 pounds pressure from a main supplying the steel works. Any pressure will work very well. The gas is made by forcing air through gasoline contained in a 60-gallon steel tank, with proper safety and check valves.

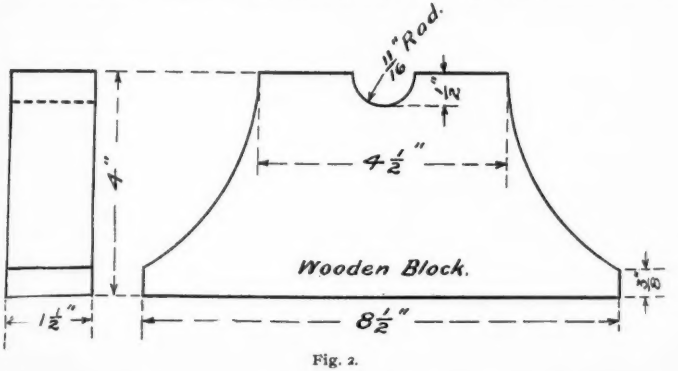

Fig. 2.

The blast-lamp materials and time will cost thirty cents each, so that it represents quite a saving over the usual burner sold, and it operates perfectly and gives an intensely hot flame. Silica may be blasted to whiteness in one minute easily and ore fusions made with great rapidity. It is admirably adapted for carbon combustions in a platinum crucible giving the bottom of the Shimer crucible an intense heat, so hot indeed that the film of carbonaceous matter can be burnt from the top of the Gooch crucible inclosed.

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REVIEW.

INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

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IN reviewing the progress of inorganic chemistry during the past year, before running over the field systematically there are two subjects of general import which should be considered. These are solutions and the so-called complex salts. The former of these properly belongs, perhaps, to the division of physical chemistry, and yet its bearing on the department of inorganic chemistry is such that some consideration of it must be regarded as within the scope of this paper. It is, however, only in the work that has been done on non-aqueous solutions that the field of the physical chemist will be trespassed upon.

Franklin has continued his studies of solutions in ammonia (this Journal, **27**, 191, 820), the latter paper containing one of the most notable generalizations recently made in chemistry, in that ammonia solutions are brought into line with water solutions. As water from the standpoint of solution is to be looked upon as a compound of $\overset{+}{H}$ and $\overset{-}{OH}$ ions, so ammonia is a compound of $\overset{+}{H}$ and $\overset{-}{NH_2}$ ions. Acids dissolved in ammonia form, as a matter of course, ammonium salts, but nevertheless they retain true acid properties. Acid amides and imides also are acids in ammonia solution, urea, for example, being ionized into $\overset{+}{H}$ and $\overset{-}{H_2N}CONH$, as well as into $2\overset{+}{H}$ and $CO\overset{=}{(NH)_2}$. The metal amides, as $NaNH_2$, act as alkalies, and neutralization reactions in ammonia correspond to those in water. Phenolphthalein can be used as an indicator. Salts hydrolyzed in water are "ammonolyzed" in ammonia; thus, $AsCl_3+3H.NH_2=As(NH_2)_3+3HCl$ ($3HCl+3NH_3=3NH_4Cl$). PCl_3 gives not $P(NH_2)_3$ but $P(NH)NH_2$, and SiS_2 gives $Si(NH)_2$. This ammonolysis need not go to com-

pletion, and when it does not we have "ammono-basic" salts, which may be more or less de-ammoniated and hence appear as amines, imines or even as nitriles, that is, nitrides. This treatment of the subject clears up in a very satisfactory way the ammonia compounds of mercury, which have so long been a stumbling block to chemists. They appear as ammono-basic salts, or mixed hydro and ammono-basic salts, occasionally with ammonia of crystallization.

Naumann has added greatly to the experimental side of non-aqueous solutions (*Ber.* **37,** 3600, 4328, 4609), furnishing data as to reactions in solutions of ethyl acetate, acetone and pyridine. Hydrogen sulphide is found by Antomy (*Gazz. chim. ital.* **35,** i, 206) as had also been noticed by Franklin, to act very differently from water as a solvent, and to rather resemble such organic solvents as ether, benzene and carbon bisulphide. Few inorganic salts dissolve; some organic substances as iodoform render the solvent a conductor, while many others dissolve without affecting the conductivity.

Continuing his work on the existence of hydrates in solution, Jones (*Am. Ch. J.* **32,** 308, 338) finds that many organic non-electrolytes form hydrates in solution, and this is especially marked in the case of glycerol. Organic acids show no such tendency. In alcohol solution some salts give evidence of forming alcoholates.

During the past year an increasing amount of work was done upon double and complex salts. Bellucci (*Z. anorg. Chem.* **44,** 168) has studied further the hexaoxyplatinates and finds that the potassium salt, $K_2Pt(OH)_6$, dissociates normally, even in very dilute solutions, and resembles closely the corresponding chloroplatinate. It forms rhombohedral crystals, isomorphous with Marignac's potassium stannate. The formula of this salt is shown (*Atti. Accad. Lincei*, Roma, (5), **13,** ii, 307, 324, 339) to be $K_2Sn(OH)_6$. These stannates are much more stable in solution than the chlorostannates, and stannates of a number of metals have been obtained by double decomposition. They begin to lose water only at temperatures considerably above 100°. By partial hydrolysis of tin tetrachloride and extraction with ether, Pfeiffer (*Ber.* **38,** 2466) obtains $SnCl_3OH$, crystallized with a molecule of water and one of ether, and similarly by alcoholysis the compound $SnCl_3OC_2H_5$ with a molecule of alcohol. These compounds appear to be formed only when the addition products of stannic chloride can split off a molecule of hydrochloric acid.

Quite a series of salts of metachlorantimonic acid have been prepared by Weinland (*Z. anorg. Chem.* **44,** 37) as well as the free acid, $HSbCl_6$, which crystallizes with $4\frac{1}{2}$ molecules of water. Weinland has also (*Ber.* **38,** 1080) further studied the double chlorides of quadrivalent antimony, preparing the (new) rubidium salt, and especially a number of isomorphous crystals with chloroplatinates and chlorostannates. This would seem finally to establish the presence of quadrivalent antimony in these salts.

In a paper upon the chloromolybdates (*Z. anorg. Chem.* **44,** 81) Weinland lays down the rule that in the metal-acids, wherever oxygen can be replaced by sulphur, it can be replaced also by chlorine and bromine, but not necessarily by fluorine. The most important types of chloromolybdates prepared by Weinland are $M'_2MoCl_4O_2$ and $M'MoCl_3O_2.H_2O$.

The compounds of sulphur tetrachloride have been investigated by Ruff and his students (*Ber.* **37,** 4513). They have confirmed the non-existence of the supposed sulphur dichloride, which is merely a solution of the tetrachloride in S_2Cl_2. This solution, formed by leading chlorine into cooled S_2Cl_2, was found satisfactory for most of their experiments. The pure tetrachloride was prepared by sealing the ordinary chloride with liquid chlorine in a tube and leaving it several days. The tetrachloride is hydrolyzed by water almost quantitatively into sulphur dioxide. Fairly stable double compounds were formed with the chlorides of quinquivalent antimony, quadrivalent titanium and tin, and trivalent iron, gold, and iodine. Less stable compounds are formed with zirconium and arsenic trifluoride.

A very thorough investigation of the double chlorides of iron and potassium and caesium has been carried out by Hinrichsen and Sachsel from the standpoint of the phase rule (*Z. physik. Chem.* **50,** 81). Both the crystals and the mother-liquor with which they were in equilibrium were analyzed. Solutions of varying composition and concentration were used, the same temperature being employed in different experiments. At 21° the only potassium salt is $K_2FeCl_5.H_2O$, while caesium forms the two salts, $Cs_2FeCl_5.H_2O$ and $Cs_3FeCl_6.H_2O$. The potassium and the first caesium salt are in accordance with Werner's theory, but the second caesium salt appears not to be.

Work upon the complex molybdates and tungstates has been continued by Smith and his fellow workers (this Journal, **26,** 1474), salts containing aluminum and bismuth, trivalent manganese and nickel, and numerous members of the rare earth group, being added to the already long list of these remarkable compounds.

In connection with Hall and Balke, Smith (*Ibid.* **26,** 1235; **27,** 1140; *Pr. Amer. Phil. Soc.* **44,** 151, 177) has done much to clear up the preparation of columbium and tantalum in a pure form, and has thrown much light upon the perplexing compounds, especially the halides, of these two metals.

Considerable work has been done by Werner (*Ber.* **37,** 4700; **38,** 923, 992, 2009) upon the cobalt bases, especially on the tri- and tetramine compounds in their hydration isomerism. He has also (*Ibid.* **38,** 893) prepared in a pure form the luteohydroxylamine cobalt base, which he finds to be easily made and very stable. A series of new compounds of hydroxylamine with the chlorides of magnesium, calcium, strontium and barium has been prepared by Antonow (*J. Russ. Physik.-Chem. Soc.* **37,** 476). By solution of metallic strontium in ammonia and the evaporation

of the excess of solvent, Roederer (*Compt. rend.* **140,** 1252) has obtained a strontium-ammonium, with the formula $Sr(NH_3)_6$, corresponding to barium-ammonium. Caesium-ammonium, $CsNH_3$, has been found by Rengade (*Ibid.* **140,** 1183, 1536) to be very unstable, decomposing slowly into hydrogen and caesium amide, even in ammonia solution. If dry ammonia gas is led over melted metallic caesium at 120°, the amide, $CsNH_2$, is rapidly formed. In the presence of air, caesium-ammonium is very readily oxidized in ammonia solution. By leading oxygen into the solution at —60° there is a gradual oxidation, and by stopping the process at intervals, three different oxides can be isolated in nearly pure condition, Cs_2O_2, Cs_2O_3, and Cs_2O_4. The reactions of sodamide are also attracting attention. Winter (this Journal, **26,** 1484) obtains very complex reactions with phosphorus pentasulphide and with yellow phosphorus. In both cases there are formed insoluble compounds which seem to be amides or oxyamides of phosphorus. Ephraim (*Z. anorg. Chem.* **44,** 185) has investigated the reactions of sodamide with a large number of inorganic compounds and finds that in general it acts as a very powerful reducing agent, all oxygen salts and most oxides and sulphides being reduced. Nitrogen is generally evolved in the reactions, which often resemble, to a considerable degree, those with metallic sodium.

The remainder of the work on inorganic chemistry in this review will be taken up in the order of the periodic system.

Group I.—Those who have had occasion to prepare sodium hydroxide in quantity from metallic sodium will appreciate a new method described by Küster (*Ibid.* **41,** 474). A crystallizing dish about 50 cm. in diameter is filled to the depth of a few centimeters with water and in the middle is placed a low, wide-mouthed flask of platinum, silver or nickel. Above this is a funnel formed out of nickel wire gauze, so supported by a tripod that the tip of the funnel is just over the mouth of the flask. In the funnel are put several hundred grams of sodium, freed from any crust. The whole is then covered with a bell jar of less diameter than the outer dish. This is prevented from reaching the bottom of the dish by a few glass rods, and with the water forms a perfect seal. The sodium begins at once to deliquesce from the moisture present and the oily solution of the hydroxide, about 40 per cent. strong, drips into the flask. The hydrogen escapes under the edge of the bell jar. Any impurity in the sodium remains on the funnel. (The sodium hydroxide is liable to contain nickel but with platinum gauze would be pure.—*Editor.*)

From the work of Treadwell and von Girsewald it appeared that in the solution of a copper salt in potassium cyanide there was present $K_6Cu_2(CN)_8'$, but investigations by Kunschert (*Ibid.* **41,** 359) by conductivity methods seem to indicate that if the potassium cyanide is in excess the anions are $Cu(CN)_4'''$, while if the proportion of potassium cyanide to copper cyanide is less

than 2.5 molecules to 1, the copper is in $Cu(CN)_3''$ anions and free potassium cyanide is present. An experiment is described by Caldecott (*Pr. Chem. Soc.* **20,** 199) on the effect of the sunlight on the solubility of gold in 0.5 per cent. potassium cyanide solution. He found that in a flask exposed to the sunlight 43 per cent. more gold was dissolved in five days than in a completely protected flask, although the exposure was only for five and a half hours each day. The temperature in the dark flask was 3.8° higher during the exposure. The cause of the increased solubility is not clear. The action of iodine on gold has been studied by F. Meyer (*Compt. rend.* **139,** 733). At ordinary temperature iodine does not act on gold, and aurous iodide is stable in a vacuum. At 50° iodine begins to act on gold and from this temperature upward the reaction is reversible. In the presence of water the reaction is also reversible and even at ordinary temperatures the gold iodide is decomposed into the elements completely, if the iodine is removed as liberated. It is possible to prepare a crystalline aurous iodide both in the dry and in the wet way.

Group II.—The recently achieved production of metallic calcium in quantity at a reasonable cost has led not merely to a study of the properties of the metal and its alloys, but also to its use in both the inorganic and organic laboratory. Arndt (*Ber.* **37,** 4733; **38,** 1972) finds its specific gravity 1.54 and its melting-point 800°, below which temperature it volatilizes. He has also examined its alloys with aluminum. That of equal parts of each metal is brilliant and stable in the air, but all, except those of high calcium content, are decidedly brittle. A similar brittleness was found by Setlik (*Chem. Ztg.* **29,** 218) to be a characteristic of the alloys with copper, lead, antimony, tin, zinc, and cadmium. Senier (*Chem. News,* **91,** 87) describes the use of calcium in lecture experiments. Calcium is well adapted to show the decomposition of water, since the hydroxide formed is precipitated. One difficulty with this experiment is the slowness with which the hydrogen is evolved, but this can undoubtedly be hastened by heating the calcium beforehand in a current of hydrogen. The calcium absorbs hydrogen, as Setlik has shown, apparently to form a hydride, CaH_2, and this decomposes water with considerable violence. The preparation of the oxide, chloride, sulphide and phosphide of calcium can readily be exhibited by heating the metal in a hard glass tube in a current of oxygen, chlorine, sulphur or phosphorus. Hackspill (*Compt. rend.* **141,** 106), by heating rubidium or caesium chloride in a vacuum with calcium, obtains metallic rubidium or caesium, which distil off and condense in crystals. Lithium cannot be obtained in a similar way, owing to its lesser volatility; it merely forms an alloy with the calcium. Beckmann (*Ber.* **38,** 904) apprehends that metallic calcium will prove a very valuable agent in organic chemistry. He describes several cases of its action as a reducing agent. It seems possible to replace magnesium by calcium in Grignard's reaction. Calcium

can further replace aluminum in the reduction of the oxides and sulphides of copper, lead, and manganese, in Goldschmidt's process. In the proceedings of the American Philosophical Society (**43,** 381), Goodwin gives a full account of the preparation of the metal, with especial reference to the economy of the process, and also describes its physical properties.

The study of radium and the other radioactive elements continues to excite an ever-increasing interest. From the wealth of material most must be omitted, but a few of the more important investigations will be noticed. Rudorf (*Z. physik. Chem.* **50,** 100), in a study of the relation between spectrum and atomic weight, discusses the atomic weight of radium. This should be, he holds, 225, as found by Madame Curie, a number which agrees well with the probable decomposition of uranium into radium and helium. If the number proposed by Runge and Precht, 258, were true, Madame Curie's radium must have contained 20 per cent. of $BaCl_2$. Further, this latter number is not reconcilable with the position of radium in the periodic table. Calculations have been made by Liebenow (*Physik. Z.* **5,** 625) regarding the amount of radium in the earth. If uniformly distributed there would be 0.0002 mg. radium per cubic meter. It may be conjectured that the outer portion of the earth contains more radium than the interior. If uniformly distributed on the surface, there would be 0.4 gram radium to each square meter, which would be equivalent to a layer of pitchblende 6 cm. in thickness. At all events there is sufficient radioactive material in the earth to keep the interior at a constant temperature. An examination of the radioactivity of a large number of minerals by Boltwood (*Phil. Mag.* [6] **9,** 599) shows that this is proportional to the uranium present, making it extremely probable that uranium is the source of radium. This ratio—radium : uranium—has been determined by Rutherford and Boltwood (*Am. J. Sci.* [4] **20,** 55) and found to be 7.4×10^{-7}. From this it appears that a ton of pitchblende contains 0.4 gram radium. An attempt to confirm the origin of radium from uranium was carried out by Soddy (*Phil. Mag.* [6] **9,** 768) who freed a kilo of uranium nitrate as perfectly as possible from radium, and sealed it in glass for 500 days. At the expiration of this period the air of the flask was 100 times as radioactive as at the beginning. While the amount found was far less than theory would have called for, Soddy considered it proved that an appreciable amount of radium had been formed from uranium in this period of a year and a half. Similar experiments by Boltwood (*Am. J. Sci.* [4] **20,** 239) gave a different result, 100 grams of purified uranium nitrate showing after 390 days no appreciable increase of activity. Boltwood suggests that the results found by Soddy may have been due to his method of freeing the uranium from every trace of radium, or to his working in a laboratory already full of radioactivity. At all

events, even Soddy's results are far smaller than would theoretically be expected. The conclusion drawn is that uranium does not decompose directly into radium, but that there is an intermediate product which decomposes very slowly. In his latest paper Boltwood (*Ibid.* **20,** 253) considers the decomposition products of the radioactive elements, especially as shown by Hillebrand's analyses of different pitchblendes. Without going into detail the following may be taken as decomposition products of radioactive elements: lead, thorium, bismuth, barium, hydrogen, possibly argon. The whole subject of radioactivity is fully discussed by Rutherford (*Arch. Sci. Phys. Nat.* Genève, **19,** 31, 125) in a paper on the actual problems of radioactivity. In this he gives a table of radioactive products, which it may be interesting to reproduce.

Product.	Half decomposed in	Emits	Properties.
Radium	1000 years	α-particles	
↓			
Emanation	4 days	α-particles	Gas of the argon type, boils at −150°.
↓			
Radium A	3 minutes	α-particles	Migrates to negative electrode, soluble in strong acids.
↓			
Radium B	21 minutes	nothing	Volatile at 500°.
↓			
Radium C	28 minutes	α-particles β-particles γ-rays	Volatile at about 1000°.
↓			
Radium D	about 40 years	β-particles γ-rays	Soluble in sulphuric acid.
↓			
Radium E	about 1 year	α-particles	Volatile at 1000°; deposited in solution on bismuth.

Radium E is possibly the active element of Marckwald's radiotellurium and is in Madame Curie's polonium. This and radium D have an atomic weight of about 200. The α-particles are quite possibly nothing other than helium, which is given off as the element breaks up. According to this hypothesis the radium, thorium, and actinium atoms are to be looked on as helium compounds.

By the fractionation of a radium-barium bromide mixture, obtained from 2500 kilos of thorianite, Hahn (*Z. physik. Chem.* **51,** 717; *J. chim. phys.* **3,** 617) has separated a new radioactive element which shows all the properties of the activity of thorium and which has been named by Ramsay radiothorium. The series of decomposition products from thorium are given by Ramsay as follows: 1, inactive thorium⇒2, radiothorium⇒3, thorium X⇒4, thorium emanation⇒5, thorium A⇒6, thorium B⇒7, ?⇒8, helium. An effort has been made by Makower (*Phil. Mag.* [6] **9,** 56) to determine the molecular weight of the radium and thorium emanation by the method of diffusion. In the case of radium emanation this was carried out with considerable accuracy, the result being about 97–99. Since the

emanation is to be looked on as monatomic, this result would place the element between molybdenum and ruthenium, as the missing next higher member of the manganese series, *i. e.*, ekamanganese. More difficulty was experienced with the thorium emanation, owing to its short existence, but its molecular weight was determined to be approximately slightly higher than that of the radium emanation.

Group III.—The existence of sodium alum has often been called in question. By mixing solutions of aluminum and sodium sulphates, Wadmore (*Pr. Chem. Soc.* **21,** 150) has prepared a compound which crystallizes like alum in octahedra and has the composition of an alum. Its solubility is slightly over one, and its concentrated solution on cooling gives an oily mass which slowly goes over into the crystallized alum. The presence of large, well-defined crystals of sodium chrome alum was reported by Morgan (*Ibid.*) from an oxidizing mixture containing sodium bichromate. It cannot be said, however, that the sodium alum question is yet finally settled.

The colors of the oxides of neodymium have been studied by Waegner (*Z. anorg. Chem.* **42,** 118) using the reflection-spectra. He finds definite spectra characteristic of the blue Nd_4O_7 and of the gray Nd_2O_3, and that the other colors are due to mixtures of oxides, these being always obtained when the heating of neodymium compounds in the air is not continued at very high temperatures for a long time. In this connection attention should be called to an excellent bibliography by R. J. Meyer (*Ibid.* **43,** 416), of the rare earths, which includes the ceria and yttria earths, thorium, and the incandescent light. While not aiming to be exhaustive, it includes practically all papers of importance.

Group IV.—Silicon-fluoroform, $SiHF_3$, and silicon-chloroform, $SiHCl_3$, have been studied by Ruff and Albert (*Ber.* **38,** 53, 2222), the former being prepared for the first time. Most attempts to prepare the fluoroform from the chloroform gave the tetrafluoride, but with stannic or titanic fluoride, chiefly fluoroform is formed. Its boiling-point, —80.2°, is peculiar in being higher than that of the tetrafluoride. Among the reactions of silicon-chloroform of interest is that with ammonia. Owing to the violence of the reaction it must be carried out in an atmosphere well diluted with hydrogen. There is formed a compound, SiNH, which, as far as concerns the elements which it contains, is analogous to HCN. In its properties, however, it bears no resemblance to prussic acid, being a white powder, subliming undecomposed below 300° at 40 mm. pressure, but decomposing readily in water with the evolution of hydrogen. It has strongly reducing properties and reacts with hydrochloric acid to re-form silicon-chloroform.

Stähler has continued his work on titanium (*Ibid.* **38,** 2619), clearing up to a considerable extent the double sulphates and

oxalates. He has also (*Ibid.* p. 2611) investigated the ammonia addition products of the halides of zirconium. Both Ruer (*Z. anorg. Chem.* **43,** 267) and Rosenheim (*Ber.* **38,** 812) have also studied zirconium, the former finding the zirconium acids to correspond to those of tin, as regards colloidal and insoluble forms. The latter has succeeded in preparing the pyridine and quinoline chlorozirconates, Pyr_2ZrCl_6, in spite of the great tendency of all salts of quadrivalent zirconium to hydrolyze. The pyridine bromozirconate was also prepared but loses hydrogen bromide in the air.

Two borides of thorium have been prepared by du Jassonneix (*Compt. rend.* **141,** 191) by the action of amorphous boron on thoria in the electric furnace. ThB_4 is a crystalline product, somewhat soluble in acids; ThB_6 is a non-crystalline substance of metallic appearance and of a reddish brown color, and is unacted on by all acids except nitric. Wedekind and Fetzer (*Chem. Ztg.* **29,** 1031) confirm this work and find that when the boron is replaced by crystalline silicon a thorium silicide is formed.

A curious instance of "tin disease" (transformation of the white modification of tin into the gray) is described by Cohen (*Chem. Weekblad,* **2,** 450) as taking place in organ pipes in St. Stephan's church at Nijmegen. These pipes date from 1776, but others only seven years old showed the same disease, indicating infection. Cohen recommends that in such instances all infected pipes should be removed. No connection could be traced between the original quality of the tin and the disease.

To the already long list of metallic peroxides from the Odessa laboratory, Tanatar (*Ber.* **38,** 1184) has added perstannic acid and quite a list of perstannates. The dry perstannic acid has the formula $HSnO_4.2H_2O$, and at 100° the formula $H_2Sn_2O_7.3H_2O$. This seems to be the compound described by Spring in 1899, without, however, its character as a peroxide being recognized.

Group V.—The action of fluorine on the oxides of nitrogen has been studied by Moissan and Lebeau (*Compt. rend.* **140,** 1573, 1621). At ordinary temperature fluorine has no action on the dioxide. No reaction with nitrous oxide occurs even at a red heat, but a reaction is induced by the electric spark, without, however, the formation of any volatile compound. The reaction between fluorine and nitric oxide is violent, but results merely in a decomposition of the oxide into its elements. At the temperature of liquid air, an excess of fluorine acts on nitric oxide with the formation of a white, very volatile solid, which condenses in part to a liquid at —80°. This is nitrofluoride, NO_2F, a very reactive gas, reacting at ordinary temperature with boron, silicon, phosphorus, arsenic, antimony, and iodine, though not with hydrogen, sulphur, selenium, or carbon. It also reacts with organic compounds, both the fluorine and the nitro-group taking part in the reaction.

It has long been known that when vitreous arsenious oxide is dissolved in hydrochloric acid and crystallizes out in octahedra, the crystallization is accompanied by luminescence. This has been investigated by Gernez (*Ibid.* **140,** 1134, 1234, 1337) and Guinchant (*Ibid.* pp. 1101, 1170). The phenomenon is due to friction between the crystals or to their fracture, and hence is a triboluminescence. This luminescence is by no means of as infrequent occurrence as has been supposed. When potassium sulphate crystallizes out of a concentrated solution, if the crystals are touched by a wire a brilliant light is emitted. About a hundred other salts were found which showed the phenomenon, among them potassium selenate and chromate, sodium bromide, iodide, acetate, and arsenate.

One of the notable developments of the past year has been the preparation of metallic tantalum on a considerable scale. Von Bolton describes (*Z. Elektrochem.* **11,** 45, 503, 722) its preparation by electrolysis and also by the action of sodium on fluotantalates. The metal unites great ductility with extreme hardness. The only effect of several days' action of a diamond drill seems to have been to slightly wear down the diamonds. (Since found an error.) It fuses only at about 2250° and gives but little dust in a vacuum on the passage of the electric current. It seems to be particularly suited for the filament of the incandescent light, requiring less than half the usual current per candle-power. The great possibilities of the metal are indicated by the fact that the firm of Siemens & Halske have already taken out 200 patents with about a thousand claims, covering the preparation and uses of the metal.

Group VI.—The interesting studies of Alexander Smith on sulphur have been continued (this Journal, **27,** 797, 979) with especial reference to liquid sulphur. It is found that there are two modifications of liquid sulphur, $S\lambda$ which is light colored and thin, and $S\mu$ which is dark and more viscid. The transition point between the two is at about 160°, and near this temperature the solution of one in the other shows great viscosity. The $S\mu$ modification seems to be the liquid form of amorphous sulphur. The polysulphides have been the subject of investigation by Küster (*Z. anorg. Chem.* **43,** 53; **44,** 431; **46,** 113) who finds that the different sulphides exist in equilibrium with each other in solution. The maximum amount of sulphur dissolved corresponds in the case of sodium to $Na_2S_{5.24}$, thus indicating the presence of a hexasulphide. The hydrolysis decreases with increasing amount of sulphur and is as follows in tenth-normal solutions: Na_2S, 86.4 per cent.; Na_2S_2, 64.6 per cent.; Na_2S_3, 37.6 per cent.; Na_2S_4, 11.8 per cent.; $Na_2S_{5.24}$, 5.7 per cent.; for NaSH, the hydrolysis is only 0.15 per cent. The constitution of the disulphide is probably $Na_2=S=S$, and that of the higher sulphides $Na_2=S.S_x$. By using caesium and rubidium, Biltz has prepared (*Ber.* **38,** 123) the pentasulphides of these elements in crystalline form. That

of rubidium is deliquescent and very unstable, but that of caesium is not hygroscopic and is soluble in 70 per cent. alcohol. The crystals are not isomorphous with those of the sulphates.

Sulphur dissolves in liquid ammonia without evolution of either nitrogen or hydrogen. The reaction is, according to Ruff (*Ibid.* **38,** 2659), $10S + 4NH_3 \rightleftarrows 6SH_2 + N_4S_4$. If the concentration of the ammonium sulphide formed is diminished, as by precipitation with silver iodide, then the reaction proceeds to the right. If the ammonium sulphide concentration is increased, as by evaporation, it goes to the left. After evaporation it is possible to recover the nitrogen sulphide, so that this is a new synthesis for this compound. Ruff has also (*Ibid.* p. 549) synthesized thionyl fluoride almost quantitatively by the action of hydrogen fluoride on nitrogen sulphide. During the year a large number of papers have appeared on hydrosulphurous acid and the hydrosulphites, but the constitution of these compounds is far from having been elucidated.

A new preparation of metallic chromium is given by Goldschmidt (*Chem. Ztg.* **29,** 56). A solution of chromium, best one of the crystallized nitrate, is exposed in a vessel of tin or of an alloy of tin to a low temperature. Both amorphous and crystalline chromium are formed in the course of a day. The accompanying precipitated chromium hydroxide can by dissolved in excess of alkali. By the reduction of chromic acid by fuming hydrochloric acid in the presence of pyridine, Weinland and Fridrich (*Ber.* **38,** 3784) have obtained crystals of the formula $CrCl_4(OH)$ $Pyr.H_2O$, which appear to be derivatives of quinquivalent chromium, corresponding to a similar bromide of molybdenum (*Z. anorg. Chem.* **44,** 115) to which Weinland assigns the formula, $MoBr_4(OH)Pyr$, this being a derivative of quinquivalent molybdenum. The name "chromanate" is proposed for derivatives of the acid $HOCrCl_4$. By the oxidation of chromates in alkaline solution with 30 per cent. hydrogen peroxide, Riesenfeld (*Ber.* **38,** 1885) obtains a series of perchromates having the formula M'_3CrO_8. These are the most highly oxidized perchromates yet prepared, are red, and stable when dry. Working similarly, but in acid solution, a series of blue salts is obtained, having the formula $M'H_2CrO_7$. These seem to be the same as those to which Wiede has assigned the composition $M'CrO_5$.

Many efforts have been made in the past, as by Berzelius, Marignac and Moissan, to prepare a hexafluoride of tungsten, but without result. Ruff has, however, succeeded (*Ibid.* **38,** 742) by the action of liquid hydrogen fluoride on tungsten hexachloride in a copper-lined iron tube, in obtaining the WF_6. It is a heavy, colorless gas, condensing to a solid at low temperature. It volatilizes at about zero. It attacks glass and is rapidly acted on by metals. Considerable work has been done by Giolitti and his students upon uranium (*Atti Accad. Lincei,* Rome, [5]

14, i, 114, 165; *Gazz. chim. ital.* **35,** ii, 145, 151, 162, 170). Giolitti has recommended precipitation with hydrofluoric acid for the determination of uranium. The precipitate he finds to contain two compounds, $UOF_2.2H_2O$, and (perhaps) UF_4. By electrolysis he has prepared $UF_2.2H_2O$ and the above-mentioned oxyfluoride, as well as a double salt of the latter with ammonium fluoride. He has further studied the equilibrium of the hydrates of uranium sulphate, and also the double carbonates of uranium and ammonium.

Group VII.—A number of fluorine compounds of the heavy metals have been described by Böhm (*Z. anorg. Chem.* **43,** 326) and crystallographical measurements made of several of them. The fluorides of mercury, copper, nickel and cobalt were made by heating the oxide with concentrated hydrofluoric acid and evaporation in a vacuum. The crystals all contain water and hydrofluoric acid, the copper salt, for example, having the formula $CuF_2.5H_2O.5HF$. By the action of an excess of (aqueous) ammonia, the mercury salt forms by ammonolysis an amine, $HgFNH_2$; the copper salt a tetrammonium fluoride; cobalt hydroxide in hydrofluoric acid gave an ammonium cobalt fluoride. Several cobaltamine compounds containing fluorine were also obtained, among them luteocobalt fluoride, $Co(NH_3)_6F_3$, and the luteocobalt chlorofluoride, $Co(NH_3)_6Cl_2F$. Moissan (*Compt. rend.* **139,** 711), in connection with his work on fluorine, has prepared pure boron and silicon fluorides for the purpose of examining their constants. The BF_3 melts at —127° and boils at —101°; the SiF_4 volatilizes at —97° without fusion, but at a pressure of two atmospheres melts at —77°. These figures were the same whether the compounds were made by the action of fluorine on boron and on silicon, or by heating fluorspar and sulphuric acid with boron trioxide and with silica.

A contribution to the chemistry of bleaching-powder is added by Tarugi (*Gazz. chim. ital.* **34,** ii, 254) who proceeds from the fact that when fully hydrated lime stands for a time in the air it shows peroxide reactions. He therefore considers that in the making of bleaching-powder the first step is the reaction of chlorine and water with the formation of oxygen and hydrochloric acid. The oxygen immediately changes the calcium hydroxide into the hydrate of the peroxide, upon which in turn the hydrogen chloride acts. Bleaching-powder is hence to be considered as the chloride of calcium peroxide. The quantitative oxidation of mercury to the bichloride by bleaching-powder supports this view. Tarugi suggests the possibility of utilizing this last reaction for the commercial production of the bichloride. He has also investigated (*Ibid.* p. 466) the pink color produced when carbon dioxide is led through a warm solution of bleaching-powder and other hypochlorites. This has ordinarily been attributed to the presence of traces of manganese. He finds that it is due, not to

manganese, but to iron, in all probability being caused by the formation of traces of calcium ferrate. Hypochlorite solutions free from iron did not show the reaction, but became pink immediately upon the addition of minute quantities of iron salts.

Mention should be made of an address on the occurrence of manganese in nature, by Bertrand (*Rev. gén. chim.* [7] **8,** 205) which treats the subject in an exhaustive manner, and especially calls attention to the importance of manganese in plant physiology. Its possible importance to animal life is very generally overlooked.

Group VIII.—Work upon the metals of the platinum group has been very meagre during the past year, but a few points deserve mention. Blondel in a long paper (*Ann. chim. phys.* [8] **6,** 81) goes over half a dozen or so classes of platinum compounds, explaining their constitution in accordance with the views of Wyrouboff. Among the compounds included are the hydroxides (oxy-acids), and their salts, sulphates, and oxalates. The views are quite antagonistic to those of Werner. A short rejoinder is made by Bellucci (*Gazz. chim. ital.* **35,** ii, 334) showing that the views of Blondel are wholly inconsistent with his own published work, especially with his physical measurements of the oxy-salts[1] (*Z. anorg. Chem.* **44,** 168). Further work has been done by Rosenheim (*Ibid.* **43,** 34) on the derivatives of phosphorus platinum chloride. A most interesting discovery is the existence of two series of isomers of which the following may serve as an example: $Cl_2.PtP(OC_2H_5)_3.C_6H_5NH_2$ and $Cl.P(OC_2H_5)_3.Pt.Cl.C_6H_5NH_2$. The former *cis* form goes over easily into the latter *trans* form, but the change is not reversible. According to Wilm rhodium possesses far greater power of condensing hydrogen than palladium, and this power varies with the method used in preparation of the rhodium. This has been re-examined by Quennessen (*Compt. rend.* **139,** 795) but not confirmed. He finds that no form of rhodium is as active as palladium, but that it rather resembles platinum in its characteristics. Further he finds no difference in rhodium prepared in different ways. Marino (*Z. anorg. Chem.* **42,** 213) has prepared the alkali series of the iridium alums as well as those of thallium. Curiously the melting-points of all the alkali alums lie between 102° and 110°, caesium and rubidium alums melting at practically the same temperature. That of the ammonium alum is just between those of rubidium and potassium. Considerable has been done by Gutbier (*Ibid.* **45,** 166, 243; **47,** 23; *Ber.* **38,** 2105, 2107, 2385) on palladium and ruthenium. Palladochlorides and bromides of a number of organic bases have been prepared as well as the palladosammine salts of the same bases. Meta- and paraphenylenediamine gave in all cases only double salts while the ortho derivative gave amine compounds. A number of ruthenium halides are described as well as the action

[1] Cf. page 402.

of oxygen on ruthenium. Of the many oxides which have been described, he finds that only RuO_2 and RuO_4 have an actual existence. The work of Wintrebert on osmium has been continued and the nitrites further investigated (*Compt. rend.* **140,** 585). The type is $M'_2Os(NO_2)_5$, and normal salts were prepared of potassium, sodium, ammonium, silver, barium, strontium, calcium, magnesium and zinc. All but the potassium salt contain water of crystallization. The free acid, $H_2Os(NO_2)_5$, was obtained in solution, but decomposed on evaporation, leaving osmium nitrite, $Os(NO_2)_3$.

Upon the inert gases, during the past year comparatively little has been done. Jaquerod and Perrot (*Ibid.* **139,** 789) have experimented with helium thermometers of quartz glass for the measurement of high temperatures. They found that above 900° the pressure in the thermometer gradually sank, owing to the diffusion of the helium through the quartz. Further investigation showed that the velocity of diffusion is proportional to the temperature. In six hours at 1100° six-sevenths of the gas had disappeared. The diffusion is noticeable at 510°, and it was shown to take place very slowly even as low as 220°. The helium thermometer made of quartz is therefore useless for high temperature work. All efforts thus far made to liquefy helium have been unsuccessful, and the same lack of success must be recorded of the latest attempts of Olszewski (*Ann. Phys.* [4] **17,** 994). Helium was compressed to 180 atmospheres at a temperature of —259°, attained by liquid and solid hydrogen. Now on reducing the pressure to a single atmosphere there was no sign of liquefaction, not even a mist. The temperature reached was 1.7° absolute. Olszewski considers it doubtful whether helium will ever be liquefied. The property possessed by wood charcoal of occluding gases very strongly at low temperatures, first utilized by Dewar, has been developed by several experimenters; Valentiner and Schmidt (*Sitzungsber. Akad. Wiss.* Berlin, 1905, p. 816) have, by means of the "fractional distillation" at low temperature of the absorbed gases, prepared from the oxygen- and nitrogen-free residue of the air, neon and helium, and from the last residues of evaporated liquid air, krypton and xenon. Using fractional absorption, Ramsay (*Pr. Roy. Soc.* **76,** A, 111) has calculated the helium and neon content of the atmosphere. There is 1 volume of neon in 80,790 volumes of air, and 1 volume of helium in 245,300 volumes of air. By weight the atmosphere contains 0.0000086 per cent. neon and 0.00000056 per cent. helium. Other experiments have shown that the free hydrogen in the air is less than $^1/_{500}$ of the amount of neon and helium taken together.

The subject of colloids is full of interest, but belongs at present rather in the field of physical chemistry. Attention may, however, be called to a paper on the nature of the colloids by Jordis (*Mon. scient.* [4] **18,** 797), to the work of Gutbier on colloidal

metals, especially of the platinum group, and especially to the papers of Whitney and his coworkers, recorded in this Journal.

WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VA., December 30, 1905.

COMPOSITION OF AMERICAN PETROLEUM.[1]

BY CHARLES F. MABERY.

Received January 1, 1906.

PETROLEUM may be regarded as one and the same substance with great variations in properties and proportions of constituents, selecting as extremes such light oils as the light colored oil found in Kansas and the extremely thick oils of Wyoming, which are nearly as heavy as water. The series of hydrocarbons that have been identified in petroleum from different fields, in this laboratory, include the following: C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}; doubtless the heavy asphaltic oils contain hydrocarbons even poorer in hydrogen.

The series of hydrocarbons which form the portions of American petroleum distilling below 350° *in vacuo*, corresponding to 475° at atmospheric pressure, are now well understood, and the members of the various series have been identified with respect to their molecular weights. But concerning the structure of these hydrocarbons, except those of the series C_nH_{2n+2} and the lower cyclic hydrocarbons, nothing whatever is known. It is reasonable to assume that the members of the series C_nH_{2n+2}, or the so-called paraffin hydrocarbons, have the open-chain structure which characterizes the lower members of this series. In the earlier literature on petroleum it was generally assumed that the ethylene hydrocarbons, series C_nH_{2n}, formed a considerable proportion of the constituents, and even after the discovery of the cyclic series C_nH_{2n}, the naphthenes, according to the earlier nomenclature of Markownikow, many writers, with no foundation on facts, still insist on the presence of ethylene hydrocarbons. It is now safe to assert that these bodies are present in any petroleum, at most in very small amounts. We have found them apparently in Canadian petroleum, but in very small quantities.

The series C_nH_{2n}, which has been identified in petroleum from many sources, is now well known as the cyclic series. In a paper published in 1902 on the composition of Pennsylvania petroleum, I purposely abstained from naming the hydrocarbons with high boiling-points of this series which we had separated and identified, for although it seemed probable that these bodies were cyclic compounds, I preferred not to suggest names for the several members until more was known concerning their structure. The names suggested

[1] Presented in abstract at the New Orleans Meeting of the American Chemical Society.

by Mr. Bogert in his summary of the results described in the paper for this Journal seem to refer those hydrocarbons to the ethylene series; but any nomenclature for these bodies must await sanction by proof of structure when some courageous investigator shall force his way into this difficult field.

An important feature of the petroleum problem is the character of the hydrocarbons which form the highest boiling portions—the so-called asphaltic hydrocarbons. The main body of these high-boiling oils is no doubt composed of series poorer in hydrogen than the methylenes, saturated cyclic compounds, consisting of the series C_nH_{2n-2}, C_nH_{2n-4}, etc. The hydrocarbons of these series also appear in the higher boiling portions of Pennsylvania, Ohio, Canada, etc., petroleum, as we have shown in papers recently published.

It does not seem clear how this problem shall be attacked. By exclusion of air and depression of boiling-points the petroleum hydrocarbons can be distilled indefinitely as high as 350°. Between 300° and 400° cracking begins, and it cannot be avoided by straight distillation even *in vacuo*. The heavy hydrocarbons seem to be so inert, by reason of their high molecular weights, they cannot retain their atomic composition at their boiling-points; they simply fall to pieces through the influence of mass. In distillation from the crude oil evidently another influence comes into operation—the effects of the oxygen, nitrogen and sulphur constituents. Since fractional distillation is the only means at present known for the separation of the homologous members of these series, the problem of their isolation becomes a difficult one.

In presenting a general summary of present knowledge concerning the composition of petroleum, it may be of interest to refer to what was known on this subject twenty years ago and when I began the work. At that time the only petroleum on the market in America was obtained from the Pennsylvania fields and the territory in Canada. The composition of Russian petroleum was then under investigation by Markownikow. As a result of their elaborate investigations on American petroleum Pelouze and Cahours had assigned the formula C_nH_{2n+2} as representing the principal series of hydrocarbons. But the high specific gravity of their distillates could not have been given by hydrocarbons separated from Pennsylvania petroleum, since these bodies give much lower values. Since the source of their products was not mentioned, it must be assumed that they came from the heavier Canadian oil, although the hydrocarbons in this oil have not the composition of the series C_nH_{2n+2} which Pelouze and Cahours deduced from their analyses, but, as we have found by results recently published, the composition of the series C_nH_{2n}. Pentane, hexane, heptane and octane had been identified by Schorlemmer, and the classic work of C. M. Warren had shown

the existence in Pennsylvania petroleum of the two series of isomeric hydrocarbons from pentane to octane. The large deposits of petroleum in northern Ohio and Indiana, Texas, Colorado, Wyoming and Kansas had not then been discovered.

In 1885, soon after the first well was drilled that yielded oil from the Trenton limestone, two oil inspectors brought me a five-gallon can of Trenton limestone oil and remained while I examined it for them. This was my first acquaintance with the sulphur petroleums. I recognized at once the large percentage of sulphur, and soon afterwards began a study of the sulphur compounds. Not long afterward I procured the Canadian sulphur oil, and carried along together the study of these products, the one from Trenton limestone and the other from the Canadian Corniferous limestone. The composition of Ohio oil has only recently been determined, with respect to the principal series of hydrocarbons, by a research completed seven years after it was begun.

At first I had no preconceived ideas as to the series of hydrocarbons which compose these crude oils, except what knowledge I had gathered from the work of my predecessors; but after the work had progressed far enough to see that the crude oils from the different fields were essentially different in certain constituents, especially in sulphur, I was inclined to look on the Trenton and Corniferous limestone crude oils as a separate species, the sulphur petroleums, and to agree with Peckham in his specific classification of the different petroleums as varieties of bitumens. But I soon became convinced that no such sharp distinctions based on composition could be drawn. Now, after these years of arduous labor, I have reached the conclusion that petroleum from whatever source is one and the same substance, capable of a simple definition—a mixture in variable proportions of a few series of hydrocarbons, the product of any particular field differing from that of any other field only in the proportion of these series and the members of the series. I arrived at this conclusion only recently, when it was found that the higher distillates from Pennsylvania petroleum contained the series C_nH_{2n-2}, which until then I had supposed was only to be found in the heavier California and Texas oils, or the so-called asphaltic oils. Results recently published show that Ohio petroleum has a similar composition.

In support of this definition I would suggest that, so far as known, all petroleums contain nitrogen and sulphur, although the proportion of nitrogen in Pennsylvania and Ohio crude oils is much smaller than that in California oil, and that the percentage of sulphur is much smaller in Pennsylvania sandstone oils—only a trace as compared with the larger amounts in the Trenton limestone, Corniferous limestone, in California and Texas oils. With this definition the distinction drawn, at least in commercial

circles, between paraffin and asphaltic oils, disappears, for Pennsylvania crude oil contains the asphaltic hydrocarbons, although I cannot assert that California oil contains paraffin. I have crystalline hydrocarbons separated from California oil, but their identity is not yet fully established. The refiner is more definite in his classification; he knows from experience that the best yield of gasoline is from Pennsylvania oil, and none from California oil. He is fully aware that it is useless to expect to obtain a respectable yield of burning oil, at least without cracking, from California or Texas petroleum, and that he cannot hope to obtain paraffin from those heavy oils. But his very heavy lubricating oils and heavy pitches and asphalts he knows can only come from the heavier petroleums, unless indeed like Byerlyte they are made by cracking.

With reference to a nomenclature of the petroleum series and hydrocarbons, no system can be safely adopted until the structure of these bodies is better understood. The aromatic hydrocarbons, benzene and its homologues, are present in all petroleums so far as examined, but in widely variable proportions. Pennsylvania crude oil contains the lower members in small amounts, but not the higher homologues. It is true that anthracene and its congeners have been described as separated from petroleum residues, but it is probable that such bodies are not present in the original oil; they are doubtless formed by decomposition during distillation. California petroleum contains much larger proportions of the aromatic hydrocarbons, especially of the xylenes and others with higher boiling-points. In one of our distillates from California crude oil so much naphthalene was present that the distillate became solid on slight cooling. This distillate came over at about 215°. The only other instance in which naphthalene has been found in petroleum was its separation by Warren and Storer from Rangoon petroleum.

The terminology of the series C_nH_{2n+2} has been well defined, and the names adopted by Kraft for the members with high boiling-points, liquids and solids, which he separated from shale distillates are applicable to the corresponding bodies in Pennsylvania crude oil. It is interesting to note that Pennsylvania petroleum alone, unless we include the analogous Berea Grit and other similar sandstone oils of southern Ohio and Virginia, contains the unbroken series up to and including the solid paraffin constituents. Although the Ohio Trenton limestone oil and the Canadian Corniferous oil contain paraffin, the former in large proportions, the liquid members of the series C_nH_{2n+2} stops with $C_{11}H_{22}$ in both Canadian and Ohio oil. The liquid hydrocarbons from there on, so far as examined, are members of the series poorer in hydrogen.

The series C_nH_{2n} has been variously named. When first

discovered in petroleum, and the hydrocarbons found to be identical with the hydrogen addition products of benzene and its homologues, the hydrocarbons from petroleum were described as hexahydro-bodies. On the discovery of a long series of these hydrocarbons in Russian oil, Markownikow suggested the name naphthenes. But when later the origin and nature of the compounds were better understood and cyclic hydrocarbons found in petroleum were shown to be identical with the synthetic products, the name cyclic was adopted for the lower petroleum hydrocarbons. These closed-chain hydrocarbons differ in their deportment towards reagents from those with an open-chain, C_nH_{2n+2}. While it is to be assumed that the series C_nH_{2n} is represented in its higher members by the methylenes, some extension of the nomenclature is necessary to include those bodies. There can evidently be but one ring with these proportions of carbon and hydrogen. For instance, the hydrocarbon $C_{12}H_{24}$ must be regarded as a long chain with the ends connected, dodecamethylene, or a lower ring with a number of side chains.

When the series C_nH_{2n-2} is reached it becomes necessary to assume a union of two rings attached by one carbon atom in each ring, or two rings having two carbon atoms in common. In the series C_nH_{2n-4} the union would be between two carbon atoms in each ring and the members should include, for instance, octohydronaphthalene which would represent the hydrocarbon $C_{10}H_{16}$. In the line of this suggestion, following the analogy of naphthalene, one side chain should be capable of oxidation, giving a derivative of phthalic acid. But the cyclic hydrocarbons seem to possess a different order of stability toward the action of reagents, and we have observed this peculiarity in bodies separated from petroleum which appear to belong to this series. For instance, the nitrogen compounds separated from California crude oil cannot be oxidized into closely allied products, the oxidation always proceeding to the formation of ultimate products, nitrogen and carbon dioxide, and we have found it impossible to control it.

The same is true of the sulphur compounds, which also appear to be cyclic derivatives. These bodies oxidize with the greatest ease to sulphuric acid, and it is difficult to control the oxidation. In general terms, the addition of hydrogen to benzene and its homologues weakens the resistive action towards reagents. This difference in stability between the series C_nH_{2n+2} and the series poorer in hydrogen appears in commercial use of the heavier products. We have recently compared the flashing point and fire test of heavy distillates from Pennsylvania crude oil and crude oils from California, Texas, etc., and it appears that the products from Pennsylvania oil have higher flashing points and fire tests than those from other fields. We have an excellent opportunity to ascertain the general application of this observa-

tion, for we have at hand samples in gallon lots of the principal lubricators made from Pennsylvania and Ohio oils on the market, and also samples of crude oils from the various fields; for example, two barrels of crude oil from Baku in the Russian field.

Products have been prepared from the crude oils to compare with Pennsylvania lubricating oils. The inferior stability of petroleum in which the series C_nH_{2n} or series poorer in hydrogen predominates has appeared in all our work on the various crude oils. For instance, the admission of air into hot Pennsylvania distillates never causes an explosion; but explosions are sure to follow the contact of air with hot distillates from other fields where the principal series is lower than the series C_nH_{2n+2}.

In combustion it is easy to see the difference in stability, in the readier separation of carbon. Then in analysis of a series, say from $C_{12}H_{24}$ to $C_{22}H_{44}$, in the lower members no carbon separates in the boat, but it gradually appears with increasing molecular weight, in larger and larger amounts.

The greater stability of the hydrocarbons C_nH_{2n+2} doubtless explains the superior quality of burning oils prepared from Pennsylvania petroleum, together with the fact of a larger proportion of hydrogen. The series poorer in hydrogen more readily separates carbon as soot and is more difficult to burn. A mixture of the two series C_nH_{2n+2} and C_nH_{2n} forms a good burning oil, and probably accounts for the excellent quality of Russian burning oil.

In the study of the physical constants of the petroleum hydrocarbons with boiling-points above 125° much remains to be done. For instance, the heat of vaporization and the specific heats have not been determined. We have done some work on the specific heats and heat of vaporization of the hydrocarbons with lower boiling-points. The heat of combustion and consequent heat of formation of these bodies is an important constant. We now have considerable data on the series C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}. Determinations have been made of the complete series C_nH_{2n+2} from Pennsylvania oil and from Ohio oil and of some other series poorer in hydrogen.

The decrease in the heat of combustion in each series with increase in molecular weights is in accordance with other observations which have shown a decrease in stability with increase in boiling-points. The series C_nH_{2n+2} decomposed with ignition in presence of air at about 350° *in vacuo*, if air is let in. The series C_nH_{2n} is much less stable. In contact with air the vapors of these hydrocarbons produced *in vacuo* readily explode even in the absence of an initial flame.

We are now occupied with the study of the decomposition products of these hydrocarbons, especially with the constituents of kerosene, gasoline, paraffin and lubricating oils. The nitrogen compounds are also under examination.

Pennsylvania Petroleum.—As mentioned above Pennsylvania crude oil contains minute amounts of sulphur and nitrogen compounds, and a small proportion of benzene derivatives, but the great bulk of the oil is composed of the series C_nH_{2n+2}, beginning with the butanes and ending with solid hydrocarbons of such high molecular weights that they cannot be determined by any method now known. We have reached the hydrocarbon, $C_{28}H_{58}$, and it is the last one of the series whose molecular weight could be determined. It is quite probable that there are as many as eight or even more of the hydrocarbons with greater molecular weight.

It has been an open question with practical oil men, and perhaps is still with some, as to whether solid paraffin is contained in crude petroleum or whether it is formed in the process of distillation. In the ordinary processes of refining crude oil, a very considerable proportion of the hydrocarbons is lost in the last stages of the destructive distillation which ends with a large mass of coke. On comparing the thin liquid crude oil with products obtained from it in refining, it would be natural for the superficial observer to reason, from the appearance of coke at the end of distillation and other heavy products, that solid paraffin should be formed in a similar way by decomposition of the liquid crude oil. But careful consideration of the nature and origin of petroleum precludes the possibility of its formation by distillation. It is true that paraffin was first obtained by Reichenbach by the distillation of vegetable and animal organic matter, and there is no question that it has been formed in a similar manner by natural processes. But petroleum must be regarded as a final product of decomposition, and while the series may be changed from one to another to a limited extent, decomposition of the constituents leads to the formation of simpler products until finally carbon is reached. Therefore, instead of paraffin as a result of decomposition of other hydrocarbons, paraffin itself is decomposed into hydrocarbons of lower molecular weight. But while this view is well supported by the facts observed relating to the nature of paraffin, we have not been satisfied with less than actual proof by experiment of its presence in crude oil. We placed several liters of crude petroleum in a large flue of the laboratory, with strong draft, and allowed it to evaporate during several weeks. Much the larger portion of the original oil evaporated, and the residue was so very thick it would scarcely flow. By careful extraction of the oil with ether and alcohol we obtained a small amount of solid paraffin, as shown by its melting-point and resemblance to ordinary solid paraffin hydrocarbons.

In another line of work we procured ten gallons of a semi-solid mass of hydrocarbons from a refining company at Coreopolis, Pa., that had been collected from the sucker rods in pumping oil and had never been distilled; this oil is very heavy, light yellow

in color and is used for the preparation of commercial cosmolines and vaselines. By cooling some of this product and crystallization we were able to separate from it a mixture of hydrocarbons closely resembling paraffin. A considerable portion of this pasty mass was subjected to fractional distillation, and a series of hydrocarbons separated with the composition of the series C_nH_{2n+2}. The oils separated by cooling and pressure gave results on analysis corresponding to series poorer in hydrogen.

We next took up the composition of the mixtures that form the vaselines and cosmolines. The refiner makes a distinction between crystallizable and uncrystallizable paraffin. But there seems to be but one form of solid paraffin hydrocarbons. Vaseline is simply a very heavy oil saturated with paraffin, and containing an excess of solid paraffin in the form of an emulsion. The oil is composed of the heavy oils of the series C_nH_{2n} and C_nH_{2n+2}, and the solid body of members of the series C_nH_{2n-2}. The so-called scale paraffin of the refiner is solid paraffin containing sufficient of the heavy oils to prevent it from a well-defined, crystalline condition.

The appearance of the series C_nH_{2n} and the series C_nH_{2n-2} in Pennsylvania petroleum distillates, as shown in a paper published recently, indicates that the so-called asphaltic hydrocarbons form a part of this petroleum with very high boiling-points. This places Pennsylvania petroleum in the same category with the heavier petroleum from such fields as California and Texas, the chief difference being the predominating series C_nH_{2n+2} in Pennsylvania oil and the series poorer in hydrogen in the heavier products. As explained above, the large proportion of the paraffin hydrocarbons in the heavier portions of Pennsylvania oil apparently renders the lubricating distillates more stable. Just what effect it has on the lubricating qualities, so far as I know, has not been completely determined. Some experiments on the very heavy lubricants from Beaumont oil have demonstrated very superior lubricating qualities.

Ohio Trenton Limestone Petroleum.—Since the first discovery of this petroleum, there has been uncertainty concerning its composition. In the preparation of commercial products, the refiner discovered essential differences between it and Pennsylvania oil, which were fully understood with reference to its refining qualities. The first serious obstacle was the large amounts of sulphur compounds that must be removed for the production of an acceptable burning oil. Innumerable patents were issued for processes which included distillation over quartz, precipitation with mercuric chloride, oxidation with potassium permanganate, and numerous other impracticable ideas that had been tried only on paper. The ordinary refiner distils over scrap iron and refines with alkaline lead oxide. From much the greater part of refining oil sulphur is removed by distilling over heated copper

oxide and the recovery of the oxide, a process that is said to have originated in Canada, but is known as the Frasch process. Probably fifty tons of sulphur daily is a conservative estimate of the amount extracted from Ohio oil and burned off into the atmosphere. It is claimed for this process that it is capable of removing the sulphur to 0.02 per cent., which is probably correct. Excellent burning oils are made from Ohio petroleum.

The composition of Ohio petroleum, so far as the portions readily distilled are concerned, has only recently been ascertained. Several years ago an examination of the sulphur petroleums, as Ohio and Canadian petroleum were then designated, showed that the series C_nH_{2n+2} formed the portions of Ohio crude oil which distilled below 212°, and the same members were discovered that had been previously identified in Pennsylvania oil, although the proportion of these hydrocarbons was smaller than in Pennsylvania oil. The proportion of aromatic hydrocarbons is higher in Ohio than in Pennsylvania oil. The lower cyclic compounds are also probably contained in larger proportion in the Ohio oil. An investigation finished not long ago on the hydrocarbons contained in the limits between 112° and 280°, at 30 mm. pressure, has identified thirteen hydrocarbons, with very satisfactory data on the proportions of carbon and hydrogen, which establish the series, and the molecular weights and indices of refraction identifying the members of the series. The following hydrocarbons of the series C_nH_{2n} were found: $C_{12}H_{24}$, $C_{13}H_{26}$, $C_{14}H_{28}$, $C_{15}H_{30}$, $C_{16}H_{32}$, $C_{17}H_{34}$. Unfortunately the distillate that should yield the hydrocarbon $C_{18}H_{36}$ was lost, although its specific gravity was ascertained before filtration.

Of the series C_nH_{2n-2}, the following hydrocarbons were identified: $C_{19}H_{36}$, $C_{20}H_{38}$, $C_{21}H_{40}$, $C_{22}H_{42}$, and of the series C_nH_{2n-4}, the hydrocarbons $C_{23}H_{42}$, $C_{24}H_{44}$, $C_{25}H_{46}$.

The change in series is attended with a greater difference in specific gravity between adjacent hydrocarbons; for instance, the last change in series is very marked, as the following table shows:

Distillate.	Sp. gr.	Hydrocarbon.	Difference in sp. gr.
224–227°	0.8614	$C_{21}H_{40}$	.....
237–240°	0.8639	$C_{22}H_{42}$	0.0025
253–255°	0.8842	$C_{23}H_{42}$	0.0225
263–265°	0.8864	$C_{25}H_{48}$	0.0022

The distillates from which these hydrocarbons were separated above 150°, 30 mm., contained a large proportion of solid paraffin. The higher fractions were solid at ordinary temperatures, but no attention was given to the solid constituents, for without doubt they are identical with the solid hydrocarbons identified in Pennsylvania oil. Much difficulty was met with in separating the liquid constituents. The distillate was first cooled to 0° and filtered, and the filtrate then cooled to —10° and again filtered.

In purifying these heavy oils they were first dissolved in gasoline, and after purification the gasoline was removed by distillation. The greater preponderance of the series poor in hydrogen in Ohio oil over Pennsylvania oil explains the higher specific gravity of Ohio crude oil. The series C_nH_{2n-4} does not appear in Pennsylvania oil within the range of distillates below 300°, but it does appear in Ohio oil. The proportions of the series still poorer in hydrogen in the residues of distillation from Ohio oil are doubtless still greater.

Canadian Corniferous Limestone Petroleum.—In the paper referred to above, the composition of the distillates from Canadian oil was explained, including the hydrocarbons $C_{11}H_{22}$ and $C_{12}H_{24}$, which were identified in the fractions 196° and 214°. This limits the series C_nH_{2n+2} in Canadian oil to the lower members. Some years ago the higher fractions were examined for the individual hydrocarbons and results obtained, not yet published, that show a continuation of the series C_nH_{2n+2}; and the hydrocarbons separated included the following: $C_{12}H_{24}$, $C_{13}H_{26}$, $C_{14}H_{28}$, $C_{15}H_{30}$, $C_{16}H_{32}$.

These bodies were identified by combustion for the series, and their molecular weights ascertained for the individual members of the series; the specific gravity of each hydrocarbon agrees closely with that of the corresponding hydrocarbon of Ohio petroleum. These values are still further confirmed by the formation and analysis of the chlorides.

The proportions of the lower members of the series C_nH_{2n+2}, which form the naphtha and gasoline in Canadian petroleum, is considerably smaller than in Ohio petroleum. The proportion of burning oil distillates is also less, and it is not possible to make from Canadian oil so good burning oil. The series C_nH_{2n} shows less stability on standing than the higher series C_nH_{2n+2}. I have samples of burning oil from Canadian petroleum that have stood ten years; they have changed from "water white," the original quality of the oil, to very dark yellow. Much larger quantities of gas are evolved in refining the Canadian oil, which is run back for heating the stills. Some paraffin is made, but the yield is small. The sulphur in the crude oil gives much trouble in refining, and it is not all removed in the burning oil. The percentage of sulphur is higher than in Ohio petroleum as a rule, usually 1 per cent. Canadian petroleum should give good grades of lubricators, but I have never examined these products.

California Petroleum.—In a paper published several years ago the composition of California petroleum oil from different sections of those fields was explained, and the principal series in the range of distillates examined, which included those below 214° in all specimens of crude oils, showed the series C_nH_{2n}.

Allusion was made in the former publication to a specimen of exceptionally heavy oil from Summerland, Santa Barbara County,

of special interest, since it came from wells sunk below the level of the Pacific Ocean at high tide. No distillates were collected from this oil below 200° atmospheric pressure. Under a tension of 60 mm. continued fractional distillation separated very heavy oils that were colorless or slightly yellow. They were purified by dissolving in gasoline and agitating with sulphuric acid, common and fuming, and the gasoline distilled off with the aid of a current of carbon dioxide. The composition of these products proved to be very different from that of the other California oils, or from any others we have examined. For instance, the fraction 210–215°, 60 mm., gave as its specific gravity at 20°, 0.9085, and the proportions of carbon and hydrogen corresponded to the hydrocarbon $C_{19}H_{34}$, or the series C_nH_{2n-4}. The higher members were the most viscous distillates that we have separated in what appears to be a pure form from any petroleum.

So far as we have carried the examination of California petroleum, no solid paraffin hydrocarbons have been found. From several fields oil has been obtained whose higher distillates on standing deposited large well-defined crystals, but unlike paraffin. From the fractions between 275° and 295°, 60 mm., separated from Torrey Cañon oil, a considerable quantity of crystals separated on standing several months that melted at 57° to 62°. These crystals were readily soluble in benzene and alcohol, and crystallized from hot alcohol on cooling, apparently in a pure form, unlike the solid paraffin hydrocarbons that are very sparingly soluble in alcohol; sufficient of this product for complete identification has not yet been obtained. The higher portions of heavy California petroleum offer an attractive field for study of the series poorer in hydrogen.

Texas Petroleum.—Much attention has been attracted by the discoveries of oil in Texas, and in some respects these deposits of oil possess a peculiar interest. The older Corsicana field yields an oil that is adapted for the preparation of a fairly good grade of burning oil, but it is inferior to Pennsylvania oil, since, as Richardson has shown, it is composed chiefly of the cyclic hydrocarbons. The heavier oil at Beaumont does not yield a sufficient proportion of burning oil distillate to make its preparation economical, but it is stated that a distillate can be separated in small quantities without cracking that can be refined into an inferior grade of burning oil. So far as examined the Beaumont oil does not contain members of the series C_nH_{2n+2}, which is essential in oils that yield the best grades of kerosene. The unique occurrence of this crude oil, underlying beds of sulphur under rather loose beds of shale, should exclude any of the most volatile constituents, such as are found in Pennsylvania oil. As we have demonstrated, the predominating series of hydrocarbons include the cyclic and condensed series. The crude oil is very heavy; it easily decomposes under distillation, but by

exclusion of air very heavy distillates may be separated without decomposition, from which superior lubricating oils may be prepared, especially of the heaviest type. The heaviest residue from Beaumont oil, if decomposition has been prevented, forms the best sort of petroleum asphalt, much heavier than similar products to be obtained from any other than California crude oil; in fact all the products to be obtained from Texas oil resemble those prepared from California oil.

The sulphur compounds in Texas oil seem to be much less stable than those in Ohio and Canadian oils, perhaps on account of their higher molecular weight. It is worthy of note that heavy petroleums, such as those from Texas and California fields, contain more sulphur than more volatile crude oils, like the Pennsylvania.

Petroleum from other fields, such as Colorado, Wyoming, Japan and South America, all partake of the properties of the heavier products from the fields in this country. The Japanese crude oils were very carefully sampled for our examination five years ago. There is promise of a great development of oil territory in South America. I scarcely believe that the sample of crude oil we examined some years ago represents the true condition of the oil fields there. The heavy petroleums are rapidly increasing in value as fuel.

California petroleum contains a larger proportion of nitrogen bases than any other, so far as known. Two per cent. of nitrogen, the amount contained in several specimens of crude oil examined, corresponds to 20 or 25 per cent. of the basic oils, or about one-quarter of the crude oil consists of the nitrogen compounds. In structure these bodies are tetra- or octahydro ring compounds in homologous series. The tetrahydro condition is shown by their instability.

It is, therefore, apparent that a similar condition of instability prevails in the cyclic hydrocarbons, and in the sulphur and nitrogen compounds from heavy petroleum. The sulphur and nitrogen bodies are found in considerable quantities only in such petroleum as is mainly composed of the cyclic compounds or the series poorer in hydrogen.

Another interesting series of bodies found in California, but not in Eastern oils, at least to the same extent, are the phenols, which are present in considerable quantities in some California oil.

Kansas Petroleum.—I have made no examinations of Kansas petroleums with reference to ascertaining the predominating series of hydrocarbons. But I have examined sufficiently numerous specimens of crude oil from the different Kansas fields to show that oils from these fields differ more widely in composition than oils from any other sections that have come under my observation. The very light, nearly colorless oil contains much gasoline and is evidently composed to a very considerable

extent of the series C_nH_{2n+2}. But in the other extreme, the heavy oils with specific gravity above 0.99 contain only a small percentage distilling below 150°, the limit for gasoline, a small percentage of burning oil, and this with low specific gravity 40–42° Bé., indicating more of the series C_nH_{2n-4}. These heavy oils are largely composed of series poorer in hydrogen, of the very heavy lubricating oils and of asphalt. So far as I am aware no other oil territory presents such a wide variation in composition as the Kansas field.

NATURAL FORMATION OF PETROLEUM.

Much as has been said on this attractive subject, a broader knowledge of facts is necessary before definite conclusions can be reached. What is known forms the basis for only one explanation concerning the formation of petroleum, and that is that it was formed from vegetable or animal matter by slow decay or breaking down from complex forms of vegetable or animal life under the influence of natural forces, with no great elevation of temperature such as is necessary for distillation.

Mendeléeff's theory of the formation from carbides at high temperatures, recently asserted with greater force on the basis of Moissan's work with the electric furnace, demands too many hypothetical assumptions, and has too little support on the basis of fact. To reason from the artificial formation of alloys and carbides in an electric furnace to the natural formation of petroleum containing nitrogen, sulphur and oxygen, in the form of hydrothiophenes, hydroquinolines and phenols, demands a too broad reach of imagination to make the connections.

Bearing in mind the fact that petroleum may now be regarded as one and the same substance whatever its source, and that the deposits in different fields are composed of the same series, differing only in the proportions of these constituents, it must be admitted that it had one origin and one only. With reference to the series of hydrocarbons, it is immaterial whether its source was animal or vegetable, for under the influence of natural agencies it could have been formed as well from one as from the other.

This question has been attacked on chemical grounds from the wrong direction. Because hydrocarbons of the marsh gas series, ethylene series or acetylene series at temperatures of decomposition form minute quantities of compounds of the aromatic series, or because hexahydroaromatic bodies are formed from the aromatic hydrocarbons by heating with hydriodic acid, to assume that these same changes were produced by natural agencies and resulted in the formation of the hydrocarbons which now constitute petroleum, together with the other constituents of petroleum, ascribes to these natural agencies a direction of action and power that we do not know they possess.

In considering our present knowledge with reference to the

natural formation of petroleum, it seems to me that the following questions must be answered:

(1) What is the chronology of petroleum, in what order were the deposits formed in different fields?

(2) Were the least volatile constituents formed from the most volatile or the reverse?

(3) What is a reasonable explanation of the formation of the other constituents of petroleum?

The first question must be answered by the geologist.

It is natural to assume that the limestones formed by the accumulation of the shell remains of animal life were deposited first from the ancient sea. The sandstones, as products of erosion from the older rocks, were deposited last. The question as to whether the different deposits of petroleum were formed in situ, or formed in other strata and by some natural agency transferred to their present location, has not, I believe, been satisfactorily answered by the geologists. In case of the limestone petroleum, it would seem that it must have been formed where it is now to be found, as Hunt and Orton have ably maintained.

The theory of distillation from some other strata is not tenable in the light of the present knowledge of the constituents of petroleum. Neither could any known constituents of plants that could form petroleum be distilled, nor could the heavier portions of petroleum be distilled; the result would be only very volatile distillates and deposits of coal or graphite. In this condition deposits of petroleum should always be accompanied by coal, or with coal in the near vicinity.

In the case of Pennsylvania and the allied southern Ohio and West Virginia petroleum, it would be a great discovery to connect these deposits with coal formations, for then the source would unquestionably be vegetable growth and would support the prevailing opinion that this was the source of petroleum of this class. It is reasonable to assume, as is now believed, that Pennsylvania oil was not formed in the sandstones, but found its way there by natural agencies from lower strata, probably the Devonian shales. The infiltration of the crude oil through sandstones would have a purifying effect. It is quite probable that the very light yellow crude oils from the Berea grit and other sandstones were filtered a second time or more into their present positions.

With reference to the source of the limestone oils, the evidence is all in favor of animal origin, and the same is true of California oil, although its formation is far more recent than that of the others. Texas petroleum has not been sufficiently studied in relation to its occurrence and composition, but it is evidently of more recent origin, like California oil.

With reference to the second question, is it more reasonable

to assume, for instance, that the solid paraffin hydrocarbons were formed from the lower members of this series, or that the lower members were formed from paraffin? On this point some experimental evidence may be brought to bear. Reichenbach obtained paraffin from both vegetable and animal organic matter. Engler obtained paraffin by the distillation of fish oil, as Warren and Storer had done many years previously.

It is very well known that paraffin breaks down very readily into hydrocarbons with lower molecular weights, but it is not possible to polymerize the lower hydrocarbons into the solid paraffin hydrocarbons. The tendency in cracking of any constituents of petroleum is toward the formation of the lower series and finally carbon in the form of coke. So far as experimental evidence and observation have shown the nature and relations of the hydrocarbons which compose the different series of petroleum, the conclusion is convincing that the lower members of the series were formed from the higher. A single break in the ring of a methylene is sufficient to form by addition of hydrogen a paraffin hydrocarbon.

In answer to the third question, as to the formation of the sulphur, nitrogen and oxygen compounds in petroleum, these bodies have evidently not been built up synthetically, but are the products of decomposition of more highly organized constituents of organic bodies. It would seem that the small proportions of these bodies in Pennsylvania oil, as compared with the larger proportions in the limestone oils and California oil, should be strong evidence in favor of a different origin; that Pennsylvania oil came from organic vegetable remains, thereby explaining the small amounts of sulphur and nitrogen compounds in this class of oils.

But I think it can be asserted as a fact that the very large proportion of nitrogen compounds in California petroleum, amounting to one-fifth or more of the total weight of the oil, can only be accounted for by accepting animal remains as the source of their formation. As a summation of what is at present known of the origin of petroleum, the following answers may be given to the questions propounded above:

(1) Petroleum containing large proportions of the volatile hydrocarbons, especially of the series C_nH_{2n+2}, such as Pennsylvania petroleum, was formed from vegetable organic matter. The limestone petroleum was formed from organic matter of animal origin.

(2) Cellulose, starch and other similar bodies in plants, and the fats and nitrogen compounds in animal bodies, by gradual decomposition with exclusion of air, gave first the heavier bodies found in petroleum and by natural agencies during long periods of time, with no considerable rise in temperature, further de-

composition included as products the hydrocarbons with smaller molecular weights.

(3) The nitrogen and sulphur constituents of petroleum could only have been formed directly from or through the agency of animal organic matter.

There is an attractive field for the chemical geologist to study, more intimately than has ever been done, the occurrence of petroleum in connection with its composition.

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COTTON SEED OIL INDUSTRY OF THE SOUTH.[1]

BY DAVID SCHWARTZ.

Received January 13, 1906.

COTTON seed oil is an oil obtained from the prolific cotton plant, which is the chief agricultural product of the South. It is obtained in the following manner:

The seed, after being freed from dirt and grit, is passed through gins to remove the greater part of adhering lint. From the gins it is passed through hullers, which cut and crack the hull of the seed. The hull is then removed from the contained meats as far as possible, by suitable machinery. The meats are then passed through rolls, and then to heaters provided with steam jackets and suitable stirring gear, where the meats are cooked, in order to allow a freer flow of oil. Finally the meats are transferred to hydraulic presses where the oil is expressed.

The products thus obtained are crude cotton seed oil and cotton seed cake, with which latter we are not here concerned.

Crude cotton seed oil is a vegetable oil, liquid at the ordinary temperature and varying in color from light red to black. It contains some moisture, often a little cotton seed meal, coloring-matter, and mucilaginous matter. It consists, aside from these impurities, of a mixture of the glycerides of chiefly oleic, palmitic and linolic acids, and small quantities of hydroxy acids, varying quantities of free fatty acids, and products entailed by hydrolytic decomposition, possibly some phosphorized fats, and the usual unsaponifiable matter.

It is seldom employed in the arts in its crude state, and its value deteriorates in this condition. For this reason it is usually refined soon after production.

Refining consists of treating crude oil with the proper quantity of caustic soda solution of suitable concentration. The caustic soda combines with the free fatty acid and other impurities above enumerated forming a crude soap stock, which on account of its

[1] Read at the New Orleans Meeting of the American Chemical Society.

greater gravity settles to the bottom of the treating tank, leaving a moist, supernatant, neutral, refined oil. This oil is transferred to other kettles, to settle, and finally to dry by gentle heating. The refining process is now complete.

This refined oil is now graded as off, prime, or choice summer yellow according to its color and flavor.

Prime summer yellow cotton seed oil must be clear, sweet in flavor and odor, free from water and settlings, and of no deeper color than 35 yellow and 7.1 red on Lovibond's equivalent color scale.

According to the rules of the Interstate Cotton Seed Crushers Association, the color examination shall be made as follows: The oil is placed in a pure white four ounce sample bottle; the depth of the oil in the bottle shall be 5¼ inches. The bottle shall be placed in a tintometer which is protected from any light except reflected white light, and the reading made at the temperature of about 70° Fahrenheit. If the oil is of deeper color than the glass standard, 35 yellow, 7.1 red, it shall not be prime.

Off oils, of course, are those that do not come up to this requirement, either in color or flavor or both, while choice oils are those considerably above prime, in color, odor and brilliancy of appearance.

The distinctive term "summer yellow" is applied to distinguish oils from "winter yellow." The latter is obtained from summer yellow by chilling and removing the separated so-called "stearine." The liquid portion is winter oil, and is generally used as a table salad oil, while the solid portion is used in lard and butter substitutes.

Aside from the distinctive differences of color and flavor of various refined oils, the latter are further classified according to their bleaching qualities. Those that bleach well are set aside for white oils and lard compounds.

The uses to which cotton seed oil has been applied have already been indicated; namely, butter substitutes, lard compounds, and salad oils. These three classes of product annually consume large quantities of cotton seed oil, and it will be readily noted that cotton seed oil is essentially an edible oil. It is, in fact, but up to a comparatively few years ago it was not in nearly as much demand for edible purposes, especially in this country, as it is to-day, and large quantities were consigned to the soap kettle on that account. While the flavor and odor of prime oil is slight and pleasant in the cold, the reverse is true when it is heated, as it must be, in cooking and frying. The disagreeable odors emitted in the kitchen created a prejudice against the use of the oil and its products.

Various deodorizing processes have eliminated this trouble,

so that to-day cotton seed oil is used in ever-increasing quantity in cooking, baking and frying, with very satisfactory results.

Among high-grade cooking oils must be mentioned "Wesson oils" which have a remarkably fine flavor and are absolutely odorless. The manufacture of these oils has undoubtedly increased the consumption of cotton seed oil for edible purposes in this country and abroad. The process is due to the ingenuity of Mr. David Wesson, of New York. We have to-day Wesson butter oils, lard oils, salad oils and cooking oils, the distinctive feature of which is the flavor.

The low grades of off oils are used for soap-making, and miner's oil principally. We have therefore the following uses for cotton seed oil:

(1) Butter substitutes.
(2) Lard substitutes.
(3) Salad oil and canning oil.
(4) Cooking oil.
(5) Soap oil.
(6) Miner's oil.

Crude soap stock, the waste product of refining, is the true source of soap produced from cotton seed oil. This soap stock contains from 30 to 55 per cent. of cotton seed oil fatty acids, besides the impurities removed from crude oil, free and combined soda and water. It is very dark in color.

It is treated in various ways. The most common method is to thoroughly saponify all fats, which operation is known as "killing foots." The impurities are then washed out, and a yellow cotton seed oil soap remains. This is used as a fulling soap, or as a mixture with other soap materials to make laundry soap. Soap powders are also obtained from the material by mixing and grinding with soda ash.

Another method of treating is to separate all fatty matter with sulphuric acid, when a black grease is obtained known as pancoline. Pancoline contains from 90 to 92 per cent. of fatty acid, and a little water, some glycerine, some coloring-matter and some insoluble matter.

This black grease is usually distilled. The products of distillation are light colored fatty acids, red oils and pitch. Light colored fatty acids are used for soap stock. The pitch is an excellent roofing and insulating material.

It is hard to say how much of cotton seed oil is used for each of the above purposes. The demand abroad varies with the oil crops of European countries; and the amount of cotton seed oil that will be used for soap purposes depends a great deal on the relative cost of tallow and oil. Probably 75 per cent. of the total crop is used for edible purposes.

In regard to the production of oil in this country we can assume that for every two bales of cotton there is produced one ton of cotton seed. With a 10,000,000 bale crop, we would therefore have in round numbers 5,000,000 tons of seed of which about 60

per cent. is crushed. The balance is retained on the farms for foodstuffs, seed and fertilizer. Assuming that one ton of seed yields on the average 40 gallons of oil, we have an annual production of 120,000,000 gallons.

For the year ending September 1, 1905, there were exported from all parts of the United States 957,984 barrels of cotton seed oil, or about 51,600,000 gallons. The balance was consumed in this country, mainly for edible purposes.

THE SOUTHERN COTTON OIL CO.,
NEW ORLEANS, LA.

NEW BOOKS.

REPORT OF THE ROYAL HIGH SCHOOL OF AGRICULTURE AT PORTICI.

This work comprises the second series of the reports of this school, and includes Volume I, covering the year 1899, Volume II, for 1901, and Volume III, for 1902. Volume I, for 1899, contains a list of all the scientific papers which have been published by professors in the school. It does not contain any monographs of a strictly chemical nature. The most interesting report in the volume, for chemists, is written by Professor Eugenio Casoria, on Enology (pages 249–265). This paper contains the methods of analysis of wines as practiced in the Agricultural High Schools of Italy.

An interesting kind of wine is produced in Torre del Greco, near Naples, called *Lambiccato*. This is a kind of sweet wine, which is made by filtering the half-fermented must in order to remove the fermenting germs, and thus arresting fermentation. This half-fermented wine is used in the north of Italy for adding to the local musts for producing very delicate and highly esteemed beverages. The composition, shown by analysis, of this species of wine, gives the alcohol content as ranging from 3.42 to 9.45 per cent.

The second volume, covering the period of 1901, contains a number of articles of interest to chemists, the most important of which deals with the waters of the Vesuvian region, giving their incrusting properties and the method of purifying. A number of analyses of Vesuvian waters is given, and methods for diminishing their incrustations on boilers are discussed.

From the data of the analyses, and from the considerations set forth, it is concluded:

(1) That the encrusting power of water is decreased, or nearly

eliminated, by the alkaline carbonates, which give rise to a powdery and non-cohesive deposit, which does not become attached to the walls of boilers, does no damage, and does not cause explosions. This fact has been found to be true with alkaline waters whose saline residue exceeds 4 grams per liter.

(2) The absence of the alkaline carbonates, in waters whose saline residue is less than 1 gram per liter, results in the formation of hard and compact incrustations which adhere firmly to the sides of the boiler with disastrous effect, causing explosions.

(3) The encrusting power is diminished in waters strongly contaminated by the process of nitrification.

(4) In the estimation of hardness of water, as a measure of its encrusting power, its temporary hardness has a fixed value, due to carbonates of calcium and magnesium, and which, expressed as the carbonate of calcium, may easily be determined in the water by means of normal or tenth-normal sulphuric acid.

(5) The use of calcium hydroxide, at a low temperature, has the effect of precipitating the calcium carbonate, while the magnesium carbonate remains in solution.

(6) The total elimination of the encrusting constituents is accomplished in the same way, at a low temperature, by means of the addition of commercial sodium hydroxide.

The results brought about by this last method are rapid, and the expense is extremely slight.

The third volume, covering the period of 1902, is devoted exclusively to the study of the difficulties which surround agricultural conditions in Italy, and does not contain anything of particular interest to the chemist, although it contains many matters of great importance to the economist and statistician.

H. W. WILEY.

THE CONDUCTIVITY OF LIQUIDS. METHODS, RESULTS, CHEMICAL APPLICATIONS AND THEORETICAL CONSIDERATIONS. By OLIN FREEMAN TOWER, PH.D., Assistant Professor of Chemistry, Western Reserve University. Easton, Pa.: Chemical Publishing Co. 1905. 182 pp. Price, $1.50.

This book offers a systematic survey of our present knowledge of electrolytic conductivity. The first few chapters describe in detail the standard methods of experimental procedure. In the later chapters the author attempts, as far as possible, to avoid paralleling Kohlrausch and Holborn's "Leitvermögen der Elektro-

lyte," by giving especial attention to results obtained since the publication of that work and to subjects not there treated. Among other subjects, separate chapters are devoted to transference numbers, the theory of dissociation, special applications of conductivity measurements, the conductivity of solutions of mixed electrolytes, and finally a welcome chapter on conductivity in non-aqueous solutions.

The author shows a wide acquaintance with the literature of the subject, though one serious omission must be pointed out. In summarizing the recent determinations of conductivity no mention is made of the work of Whetham on aqueous solutions at the freezing-point.[1] The author does not claim to give a complete review of work appearing after the year 1903. Thus some important investigations of more recent date, such as the research of Noyes and Coolidge on the conductivity of aqueous solutions at high temperatures, are omitted.

The author is in general careful in his statements of fact but an occasional error may be found. On page 133 it is stated that the conductivity of pure metallic oxides is not affected by the addition of other metallic oxides, while the experiments of Nernst and his students prove just the opposite conclusion. On page 40, where the value for the specific conductivity of pure water is given, the unit is the specific conductivity of mercury, and not the reciprocal Siemens unit as stated.

Unfortunately, some of the definitions and many of the theoretical discussions can hardly be regarded as satisfactory. Here vagueness of style frequently obscures the meaning. This is particularly marked in the chapter entitled "Influence of Temperature and Pressure."

However, the work is primarily a compilation of recent measurements of conductivity, many of which have been recalculated in rational units and put in tabular form, and as such it will prove a handy book of reference, especially to those who lack a reading knowledge of German. A satisfactory index is appended.

GILBERT N. LEWIS.

THE PRODUCTION OF ALUMINUM AND ITS INDUSTRIAL USE. By ADOLPHE MINET. Translated, with additions, by LEONARD WALDO, S.D. (Harv.). New York: John Wiley & Sons. 1905. Price, $2.50.

This little volume will prove to be very entertaining to those

[1] Z. physik. Chem. 33, 344 (1900).

who are interested in the problems of electro-metallurgy. It presents the views of one who for years has occupied himself with the solution of a single problem. It gives, too, what may be termed the French view-point. It keeps constantly in the front what has been done in France, and this fact instead of detracting, really enhances its value to those who wish to study the question in the broadest way. It might almost be said that of the very many methods which have been proposed for the separation of aluminium but three, those of Minet, Heroult and Hall, are discussed at any length, and are apparently regarded as possessing any value. It is true that Minet alludes to the numerous methods which have been suggested from time to time. A few of these touch closely upon his own thought; he naturally devotes the greatest attention to the methods of Heroult and Hall, because they come nearest to his own ideas.

In its German dress, this little volume of Minet received rather sharp criticism. If one considers all the facts in the case, this was not deserved. One should bear in mind that an author is apt to think most highly of his own efforts, the efforts of his friends, or those of his countrymen. So that if Minet failed to fully credit all who have made studies of the electro-metallurgy of aluminium, he should not be criticized too severely, but rather be looked upon as giving us the view-point of a Frenchman. By combining a series of such view-points, offered by representatives of various countries, we get a very excellent picture of the problem as a whole.

The translator will find a few things which he will, no doubt, correct in the future edition of the book. It is a little awkward to speak of caustic sodium hydrate when one has in mind NaOH. Several other slips of this kind will be noticed throughout the text.

The appendix contains a very interesting review of the aluminium problem, by the translator, in which he has strongly emphasized the fact that to the efforts of the Cowles brothers many later procedures are indebted for their inception and development.

No student of chemistry who peruses this little volume of Minet will lay it aside without the thought that it contains much which is new, suggestive, and helpful. It is worthy of the study of all who are interested in electro-metallurgy, in particular or in electrochemistry in general. EDGAR F. SMITH.

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FABRICATION DES ALCOOLS: 2^{e} PARTIE: TABLES D'AUGMENTATION ET DE RÉDUCTION DES DEGRÉS ALCOOLIQUES. By P. Dussert. Paris: B. Tignol. 228 pp. 4 fr. 50.

FORMULAIRE GÉNÉRAL DES RÉACTIONS ET RÉACTIFS CHIMIQUES ET MICROSCOPIQUES. By R. Roche. Paris: B. Tignol. 356 pp. 10 fr.

EINFÜHRUNG IN DIE PRAKTISCHE CHEMIE. By Professor Fel. B. Ahrens. (2 Tle. in 1 Bd.) Unorganischer und organischer Teil. Stuttgart: E. H. Moritz. 1905. 160+144 pp. 2 Marks.

CHEMIE DER ALICYKLISCHEN VERBINDUNGEN. By Ossian Aschan. Braunschweig: F. Vieweg & Sohn. 1905. 45+1163 pp. 42 Marks.

BLEIVERGIFTUNGEN IN HÜTTENMANNISCHEN UND GEWERBLICHEN BETRIEBEN. URSACHEN UND BEKAMPFG. Hrsg. vom k. k. arbeitsstatist. Amt. im Handelsministerium. 2. Tl. Bericht über die Erhebgn. in Bleiweiss- und Bleioxydfabriken. Wien: A. Hölder. 1905. 7+37 pp. Marks 2.60.

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